SYNTHESIS OF DONOR-ACCEPTOR TYPE ELECTROACTIVE MONOMERS BEARING PYRROLE AND SELENOPHENE AS THE DONOR MOIETIES AND THEIR POLYMERS

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SYNTHESIS OF DONOR-ACCEPTOR TYPE ELECTROACTIVE MONOMERS BEARING PYRROLE AND SELENOPHENE AS THE DONOR MOIETIES AND THEIR POLYMERS

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ABSTRACT

THE SYNTHESIS OF DONOR-ACCEPTOR TYPE ELECTROACTIVE MONOMERS BEARING PYRROLE AND SELENOPHENE AS THE DONOR MOIETIES AND THEIR POLYMERS

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Synthesis of new electroactive monomers are highly desired since these compounds can be utilized as active layers in many device applications such as ECDs, LEDs and solar cells. Pyrrole and selenophene bearing polymers were also proven to be excellent candidates as electrochromic materials. Benzothiodiazole can be coupled to to pyrrole and selenophene yield materials that can be polymerized to give donor acceptor type polymers. These donor-acceptor type materials; Poly(4,7-di(1H-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole P(PYBTPY) and poly(4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole P(SEBTSE) were synthesized via bromination, stannylation and Stille coupling reactions. Electrochemical and electrochromic properties of the polymers were examined in detail.

Keywords: Electrochromism, Donor-Acceptor Polymers, Pyrrole, Selenophene

ÖZ

DONÖR GRUP OLARAK SELENOFEN VE PİROL İÇEREN DONÖR AKSEPTÖR TİPİ ELEKTROAKTİF MONOMERLERLERİN VE POLİMERLERİNİN SENTEZİ

Buğra Epik
Yüksek Lisans, Kimya Bölümü
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Elektroaktif monomerler elektrokromik cihazlar, LED ve güneş pilleri gibi birçok cihaz uygulamalarında aktif yüzey olarak kullanılırlar. Pirol ve Selenofen içeren polimerler elektrokromik komponentlerden biri olarak işlev görürler. Benzotiodiazolün, selenofen ve pirol birimleri ile eşleştirilmesi ile sentezlenen monomerler donör akseptör tipi polimerlerin eldesinde kullanılabilir.Bu donör akseptör tipi monomerler poli(4,7-di(1H-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole P(PYBTPY) and poli(4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole P(SEBTSE) sırası ile brominasyon, stanilasyon ve Stille-coupling reaksiyonları ile sentezlenmiştir. Polimerlerin elektrokimyasal ve elektrokromik özellikleri ayrıntılı olarak incelenmiştir.

Anahtar Sözcükler: Elektrokromizm, donör-akseptör polimerler, pirol, selenofen

To my beloved family

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INTRODUCTION

1.1 History of Conducting Polymers

Conducting polymers are organic materials which posses electronic, electrical, magnetic and optical properties of a metal while retaining the mechanical properties of the conventional polymers. Therefore, they are called as “synthetic metals” (1).

Conducting polymers have unusual electronic properties, such as low energy optical transition, low ionization potentials and high electron affinities which are caused by delocalization of electrons. Delocalization is increased with the conjugation. Conducting polymers are consisting of sp^2 hybridized carbon backbones. The overlapping of Pz orbitals increase the delocalization among the chain hence, conductivity increases.

Conducting polymers become famous after the excellent work of Shirakawa in which high electrical conductivity of polyacetylene was achieved upon doping. In 1977, Shirakawa discovered the conductivity of PAc films upon a treatment with iodine, chlorine or bromine vapor, and “doped” form of PAc was found to possess a conductivity of 103 S/cm. Normally the electrons in the bonds remain localized and cannot carry electric current, but when the polymer was doped with strong electron acceptors such as iodine, it began to conduct nearly as a metal, with conductivity 10^{11} times higher than pure polyacetylene (PA) (2). Before this research, polymers were known as insulators.

As a result of this breakthrough work the 2000 Nobel Prize in Chemistry went to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa “for the discovery and development of conductive polymers” which reflects both research and practical importance of conducting polymers and their applications in modern science and daily life.

Some common applications are electrochromic rearview mirrors (3), polymer light-emitting diodes (4), organic solar cells (5), gas sensors (6), thin-film transistors (7) and electrochromic devices (8).

Further research in the field has led to other conducting polymers, like polythiophenes, polypyrroles and many others.

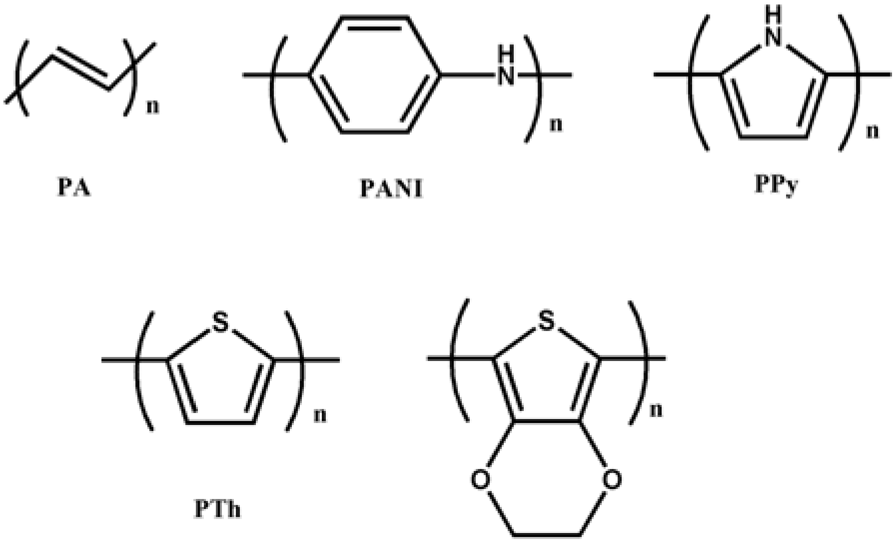


Figure 1.1 Common conducting polymers. PA, poly(acetylene). PANI, poly(aniline). PPy, poly(pyrrole). PTh, poly(thiophene). PEDOT, poly(3,4ethylenedioxythiophene).

Synthetic chemists were interested in synthesizing new conducting polymers with enhanced properties in the early 1980s. At this area, polypyrrole (PPy) was discovered via oxidative electropolymerization as a homogenous, free-standing film. Polypyrrole shows high conductivity (100 S/cm), it is flexible and stable against humidity and oxygen (9). Additionally polythiophene (10), polyaniline (11) and their derivatives such as poly(3,4-ethylenedioxythiophene) (PEDOT) were studied widely for their superior properties like low oxidation potential and ease of processability compared to PAc allocating for more variety of structures.

1.2 Band Theory

The conduction mechanism and electronic structure are easily explained with the help of band theory. Depending on the relative separation of difference between energy states occupied and unoccupied, materials can be defined as metals (conductors), semiconductors and insulators.

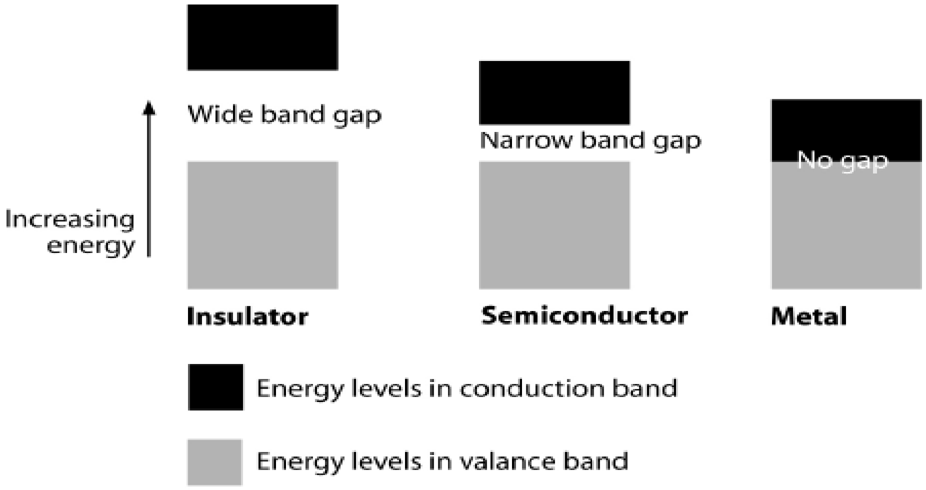


Figure 1.2 Band structures of insulator, semiconductor, and conductor (metal).

The main difference between these materials is related with the gap between the valence band (VB), the highest occupied electronic level, and the conduction band (CB) the lowest unoccupied electronic level. The energy spacing between the highest occupied and lowest unoccupied band is called the band gap. The width of the band gap determines the intrinsic electrical properties of the material. In metals, electrons can simply flow through the material since there is no energy gap between the valence and conduction bands. Insulators are illustrated by a comparatively large energy gap between the two bands which leads to the low conductivities observed in these substances. In semiconductors the valence band is separated from the conduction band by an energy gap varying from 1 - 4 eV (Figure.1.2). This range of energies associates to the visible spectrum and is correlated with electronic transitions; therefore these materials often show intense color. (12)

The band gap of a conducting polymer can be calculated using the absorption band edge in the UV-vis spectrum of the polymer. The absorption band edge is the minimum energy needed to excite an electron to the conduction band from the valence band, which represents the real energy gap between these two bands. However, sometimes the absorption maximum is used and referred as the band gap.

Another method to calculate the band gap is to measure the oxidation and reduction potentials of the polymer. The energy difference between oxidation and reduction potentials gives the band gap (13).

1.3 Conduction in Conducting Polymers

In conjugated polymer chains, conductivity is achieved by the π-orbitals of the repeating units throughout the chain (14). The HOMO and LUMO orbitals of PA are shown in the Figure 1.3 with increasing number of repeating units among the polymer chain.

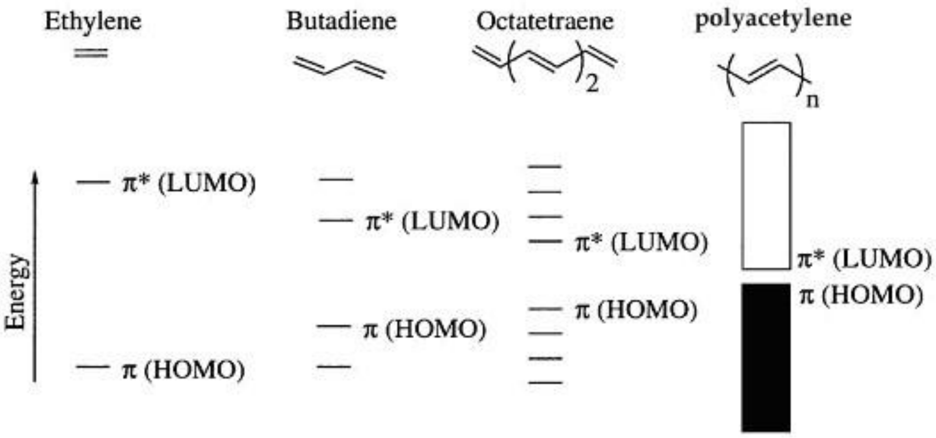


Figure 1.3 Generation of bands in conjugated polymer (PA).

Inorganic semiconductors such as Si or GaAs are three dimensionally bonded materials, with the fourfold (or sixfold, etc.) coordination of each atom to its neighbors through covalent bonds. On the other hand, conjugated polymers have two-fold coordination which makes these systems generally more susceptible to structural distortion. As a result, the dominant electronic excitations are inherently coupled to chain distortions. Since it is energetically more favorable for conjugated polymers to localize these charges, new energy levels are formed within the otherwise forbidden band gap.

1.3.1 Doping

To control the electrical conductivity of a polymer over the range from insulating to highly conducting (metallic) state is possible. This process is called doping (15). Different conductivity levels between the undoped (insulation and semiconducting) and fully doped (highly conducting) form can be easily obtained by adjusting the doping level (16) (Figure 1.4).

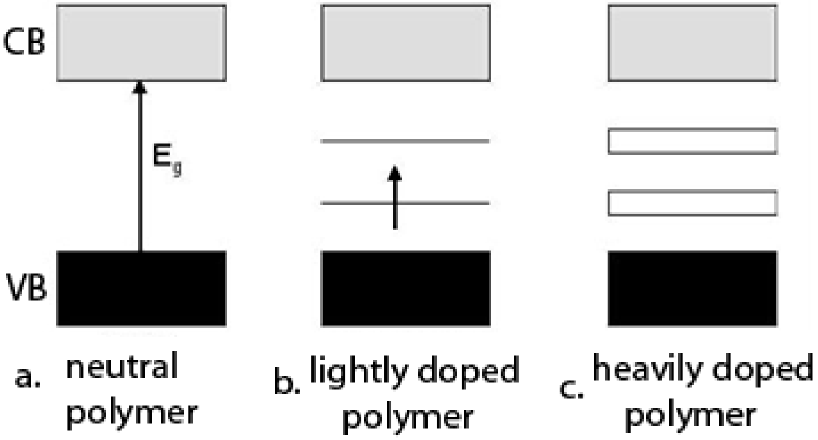


Figure 1.4 Band model of (a) non-doped, (b) slightly doped, and (c) heavily doped conducting polymers.

Doping of conducting polymers has been achieved by redox processes. This process consists of partial addition (reduction) or removal (oxidation) of electrons to or from the polymer backbone. It is known that doping and dedoping are generally reversible and do not change the chemical nature of the original backbone (Figure 1.5). Both doping and undoping processes involve dopant counterions which stabilize the doped state (17).

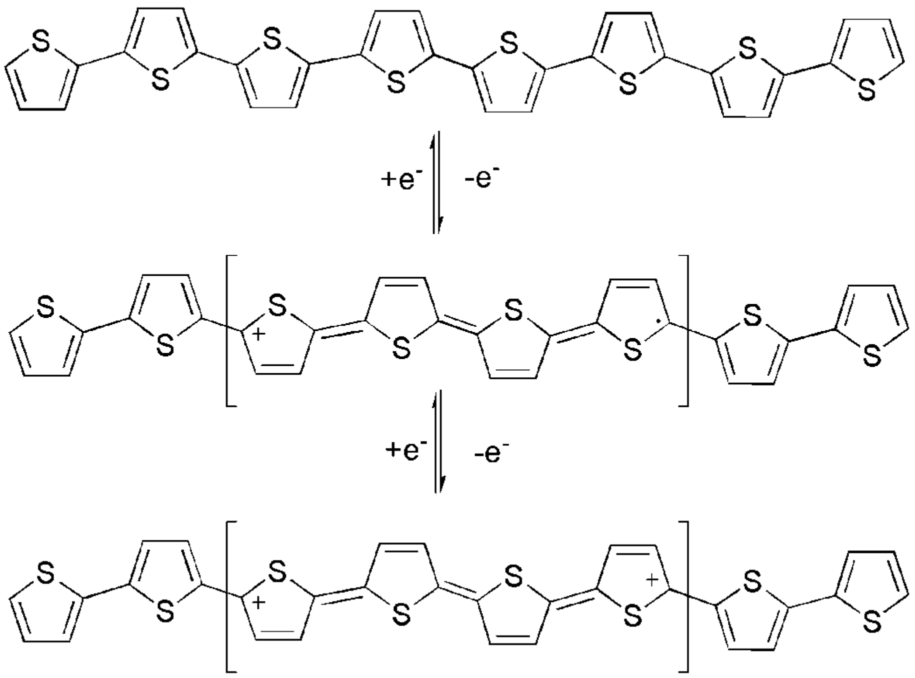


Figure 1.5 Reversible doping-dedoping process of polythiophene

The doped structures of conducting polymers can produce *solitons, polarons* and *bipolarons* on the chains with higher energies than the neutral polymer.

1.3.2 Solitons, Polarons, Bipolarons

When polymers are doped, conjugational defects occur in the polymer chain. These defects in the polymer act as the charge carriers which are radicals, anions, cations or combinations of these. These combinations are termed as solitons, polarons, and bipolarons (18).

Oxidation of the polymer breaks one double bond leaving a radical and a positive charge on the polymer chain, which is referred as polaron. Soliton is another charge defect which is classified into three categories: Neutral soliton, positive soliton and negative soliton. In neutral soliton, energy level is singly occupied and therefore, the spin has the value of ½. Neutral solitons have spin but no charge. The positively soliton is obtained by the insertion of acceptor band (p-type doping) or electrochemical oxidation, where an electron is removed. By the insertion of donor band(n-type doping), an electron is added, which results in the generation of negatively charged soliton.

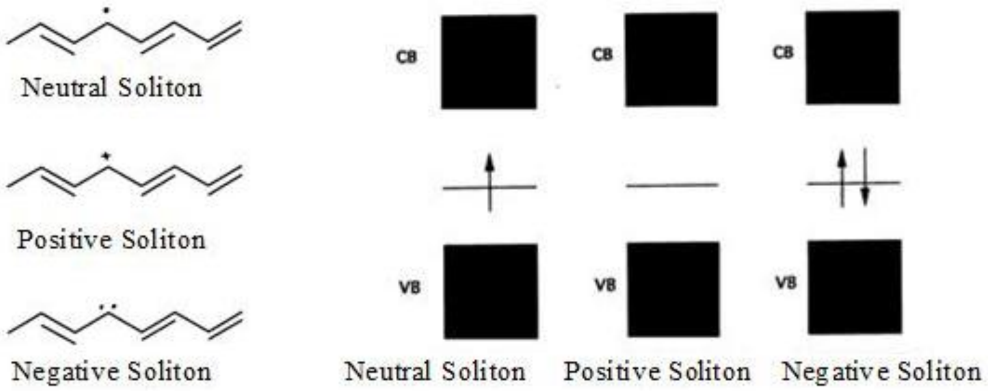


Figure 1.6 Soliton structures of polyacetylene

In the case of polypyrrole (Figure 1.7), chemical oxidation removes an electron from the π-system of its backbone creating an unpaired electron with spin ½ (a free radical) and a spinless positive charge (cation). The radical and the cation are coupled to each other via a local bond rearrangement, creating a polaron which appears in the band structure as a single unpaired electron possessing charge and spin.

The formation of two new electronic states, which appear within the valence and conduction band of the polymer, takes place as a result of this deformation.

Further oxidation of the polymer creates dications in the polymer. An electron can be removed either from the polaron or from the remaining neutral portion of the chain. Formation of bipolaron is thermodynamically favorable since the formation of a bipolaron produces a larger decrease in ionization energy compared to the formation of two polarons (19). These new empty bipolaron states are also located symmetrically within the band gap. Further doping creates additional localized bipolaron states, which eventually overlap to form continuous bipolaron bands at high enough doping levels.

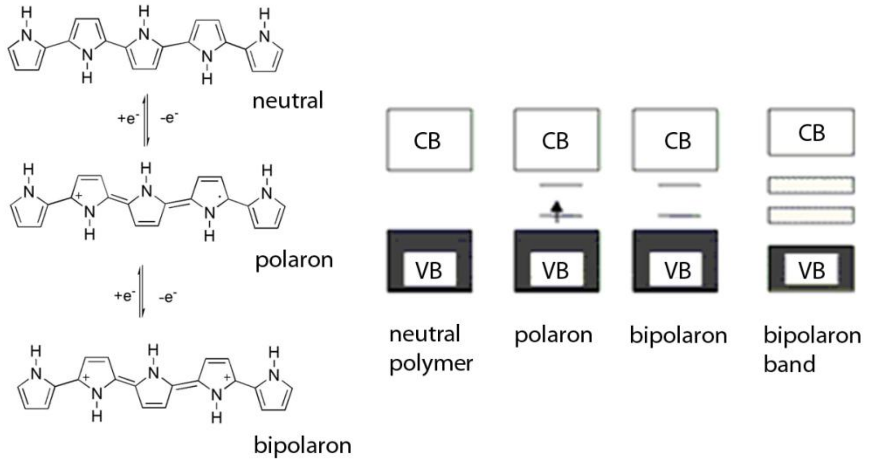


Figure 1.7 Charge carries in PPy and its corresponding energy bands in the mid gap

1.4 Chromism

Chromism for a material is defined as the reversible change in materials' color, absorbance or reflection resulting from an external effect. The effect which causes chromism can be temperature change (thermochromism), electromagnetic radiation (photochromism), change in pH (halochromism), mechanical (piezochromism) and electrochemical (electrochromism) (20)

Electrochromism, the most commercially utilized type which might have various potential applications, including displays, rear-view mirrors, smart windows, active optical filters and computer data storage is discussed in detail in the following section.

1.5 Electrochromism

Electrochromism is reversible and visible change in color or more conveniently in optical properties upon applied potential which leads to oxidation and reduction. Switching between the states results in the generation of different electronic absorption bands in visible region. The color changes between a transparent state and a colored state, or between the two colored states. The electrochromic materials may exhibit several colors (multichromic) and the process is called as multicolor electrochromism (21).The important characteristics of electrochromic materials are the switching times, the contrast ratios between different states, coloration efficiency meaning injected ejected charge per unit area, electrochromic memory and long term stability. For an electrochromic material, the electrochromic memory is the ability to remember color in the absence of current and the long term stability is the ability to retain electrochromic properties over a large number of switching cycles.

There are basically three categories of electrochromic materials; metal oxide films, molecular dyes and conducting polymers. Among electrochromic materials, transition-metal oxides, especially the high band-gap semiconductor tungsten oxide, WO_3, have been widely studied over the past 30 years (22-24). It is convenient to explain electrochromism in tungsten oxide by referring to the simple reaction

$$\underset{\text{(transparent)}}{WO_3} + xM^+ + xe^- \rightarrow \underset{\text{(blue)}}{M_xWO_3}$$

Where $M^+ = H^+$, Li^+, Na^+, or K^+ (21).

Tungsten oxide has a cubic structure which may be simply described as an "empty-perovskite" type formed by WO_6 octahedral that share corners. Tungsten trioxide, with all tungsten sites have the oxidation state of six, is a transparent thin film. On electrochemical reduction, W_V sites are generated to give the electrochromic (blue coloration) effect. WO_3 is a cathodically ion insertion material. The blue coloration in the thin film of WO_3 can be reversed by the electrochemical oxidation. Many other inorganic materials have received attention for their electrochromic properties such as Prussian Blue, oxides of V, Mo, Nb, and Ti (cathodically coloring), and oxides of Ni, Co, and Ir (anodically coloring) (25).

Other EC materials include organic small molecules, such as the bipyridiliums. They are known as viologens and are a class of materials that are transparent in the stable dicationic state (26). Reductive electron transfer to viologen dications forms radical cations. Generally the viologen radical cations are intensely colored, with high molar absorption coefficients, owing to optical charge transfer between the (formally) +1 and zero valent nitrogens. N-substituted viologens such as heptyl viologen and polyviologens show thin film electrochromism (27). Composite systems, where organic molecules are adsorbed on mesoporous nanoparticles of doped metal oxides have been reported because of their improved electrochromic properties (28-29).

1.5.1 Electrochromism in Conducting Polymer

Conjugated polymers as a class of EC materials have received attention due to their ease of processability, (they can be easily prepared by simple chemical, electrochemical polymerization and the films can be obtained by simple techniques such as dip coating, spin coating, etc), rapid response times (less than 1 second), and high optical contrasts and the ability to modify their structure. Moreover, by adjusting the electronic character of the π system along the neutral polymer backbone, the π-π* transition can be adjusted across the electromagnetic spectrum from the UV, through the visible and into the near-infrared (30). In the light of these advantages, conjugated polymers have gained popularity in common applications of EC materials include a variety of displays, smart windows, optical shutters, and mirror devices.

Derivatives of PPy, PTh, PEDOT, and PANI which have been studied most recently display electrochromism in thin film form. The working principle of electrochromism in conjugated polymers is that reversible insertion and extraction of ions through the polymer film upon electrochemical oxidation and reduction change the conjugated polymer's π-electronic character. These polymers show semiconducting behavior with an energy gap (Eg) in their neutral states. The band structure of the neutral polymer is modified upon electrochemical or chemical doping ("p-doping" for oxidation and "n-doping" for reduction) that results lower energy intraband transitions and creation of charged carriers (polarons and bipolarons). These charge carriers have the responsibility for increased conductivity and optical modulation. Generally spectroelectrochemical experiments are most vividly used to illustrate the doping process and the resultant optical changes in conjugated polymers. According to literature, the expected transitions in a conjugated polymer can be explained by following explanations (31). In the neutral state the polymer exhibits single broad transition from the valence band to the conduction band (π to π *). The energy difference between these two levels is the band gap (Eg), and it is measured as the onset of the π to π * absorption in the neutral state of the polymer. A new absorption band in the near-IR region forming at the expense of the π-π* transition upon oxidation (p-doping), which is related to polarons (radical cations) generated along the polymer chain. Upon further electrochemical oxidation, the intensity of both of the π - π * transition and the polaron absorption decrease, while a new absorption band peaked in the near-IR beyond the range of the spectrophotometer, arises. This absorption is assigned to the bipolaronic (dication) state of the conjugated polymer. Such optical and structural changes make polymers change color and that makes EC polymers potentially useful in applications.

1.6 Spectroelectrochemisty

In order to investigate the electronic structure of the polymers, along with the optical changes arising from during redox switching which are important for electrochromic applications, optoelectrochemical analyses were carried out (32). It offers information on the material’s band gap and interband states produced upon doping. In addition it gives some information about the color through the location of the absorption maxima and the ratio of peak intensities if the material shows fine structure on the main π-π* peak.

1.7 Electrochromic Contrast and Switching Speed

Electrochromic contrast is one of the important parameters for evaluating an electrochromic material. Electrochromic switching studies are carried out to observe absorbance alterations with time through repeated potential stepping between reduced and oxidized states to obtain an insight about the optical contrast. It is often reported as a percent transmittance change (ΔT %) at specified wavelength where the electrochromic material has the highest optical contrast (33).

Switching time is the time required to switch between bleached and colored states. The switching speed of electrochromic materials is affected by factors such as the morphology of the film, the ionic conductivity of the electrolyte, and accessibility of the ions to the electroactive sites.

1.8 Colorimetry

When light hits our eyes, it is absorbed by photoreceptors called the rods and cones on the retina and transformed into nerve signals translated into a perception of color by the brain. Many of the existing color systems have three coordinates because humans have a three-dimensional color space. Three pixels with red, green and blue (RGB) color are used to span color space in electrochromic materials. The RGB color system is practical for forming a display; however it is actually not a good description of the full color space accessible with human eyes.

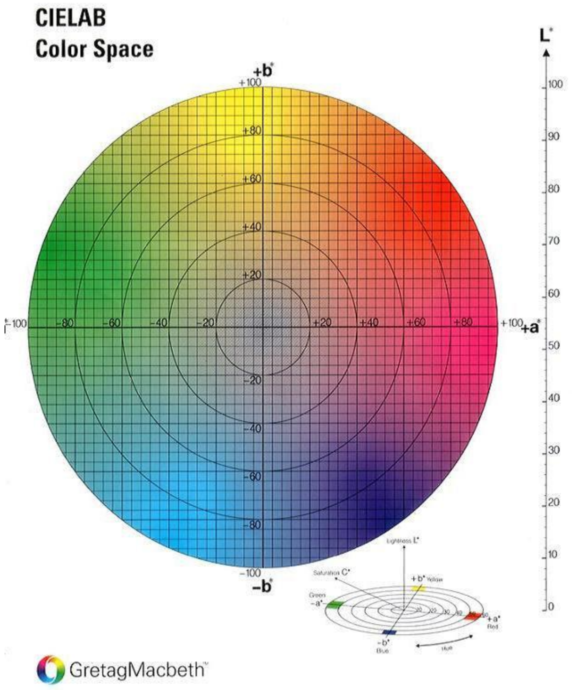


Figure 1.8 CIE LAB color space

In 1931, the International Commission on Illumination (Commission Internationale de l'Eclairage, CIE) developed a model defining colors by three coordinates by *X*, *Y* and *Z*, corresponding to different biological receptors in the human eye (Figure 1.8) The model was improved in 1976 to be able to further adapt, to the way the human eye perceives colors, by introducing the CIE L, a, b color system, where the nonlinear behavior of the eye is considered. In the CIE L, a, b system the color is represented by L, a and b coordinates. L gives the luminance (lightness), while *a* refers to hue, dominant wavelength, or chromatic color, and *b* known as the saturation, chroma, tone, or purity. L has values from 0 (dark) to 100 (light), ranges from –128 (green) to 127 (red) and b from –128 (blue) to 127 (yellow).

Applications work with two color models, each one, for its own purposes. The additive model is based on mixing the light, while the subtractive model is based on mixing the pigments. In a simple way, we work with the additive model (RGB) when preparing contents to be displayed on tv, internet, mobile or any light source. When working for printing, we work with the subtractive model (CMYK).

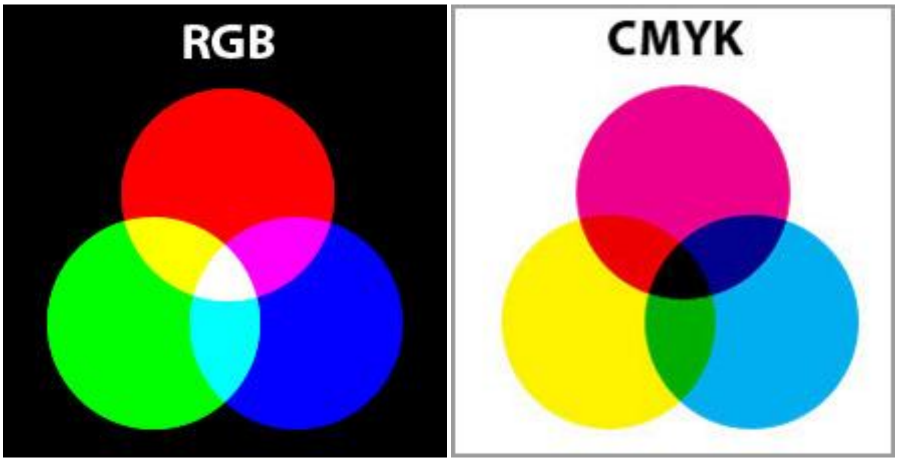


Figure 1. 9 RGB and CMYK color models.

Notice something interesting: the mixing of RGB creates CMY colors, while the mixing of CMY creates RGB colors. And again, the mixing of light colors creates white and the mixing of pigment colors create black.

1.9 Donor-Acceptor Theory and Low Band Gap Systems

π-Conjugated polymers with donor-acceptor moieties have gained attention due to the facility of ready manipulation of the HOMO/LUMO levels (electronic structure), which leads to small band gap semiconducting polymers and enhance third-order nonlinear optical properties of the materials (34-35). Minimizing the band gap is an important goal since small band gaps maximizes conductivity of the neutral CPs.

Polymers having band gaps greater than 2 eV are called mid- to high band gap, those having lower than 1.5 eV are considered as relatively low band gap materials. There are few examples available in the literature with band gaps below 0.8 eV (36).

Bond-length alternation is the difference in the length of single and double bonds along the polymer backbone. The quinoid form has a much lower band gap than the aromatic state.

A number of researchers have utilized many different methods to achieve highly planar low band gap systems because the higher the torsion angle between adjacent rings the larger the band gap of a system (Figure 1.9).

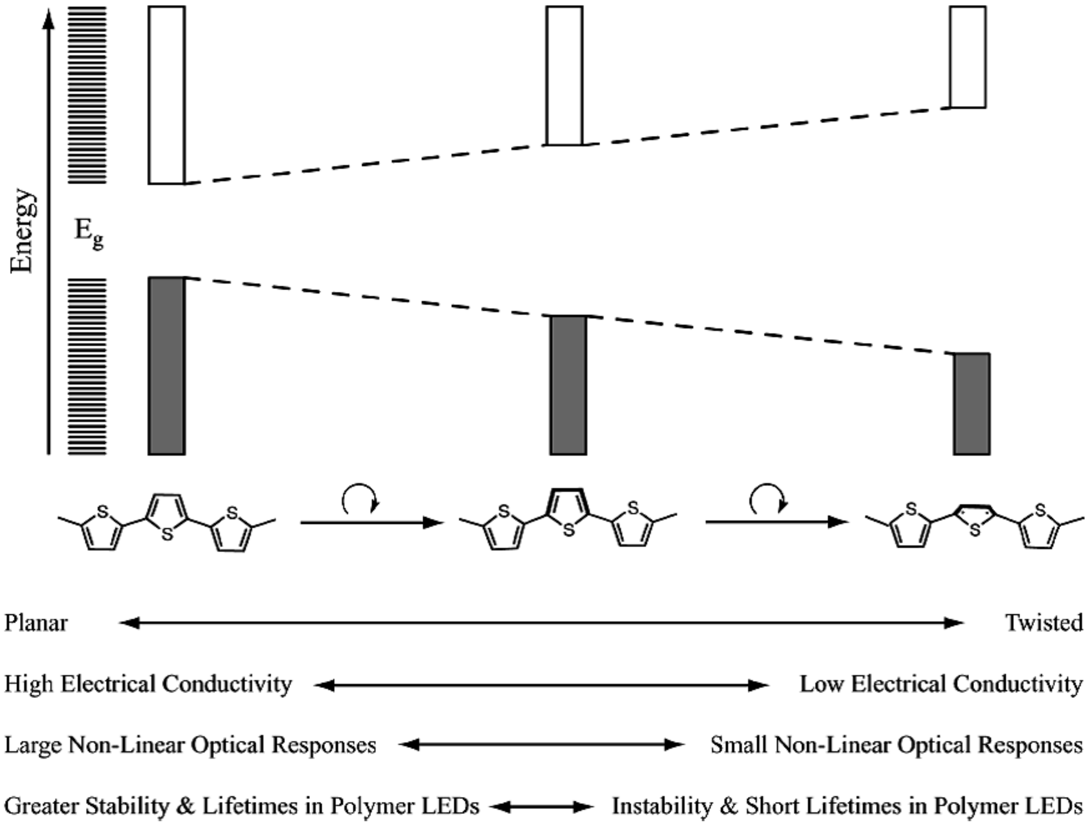


Figure 1.10 Planarity effects on band gap and the electrical and optical properties of conjugated polymers

PITN is a notable example of one of the earliest low band gap polymers, since there exists a competition between aromatic and quinoid geometries in the polymer structure (37). As it is mentioned in the section 1.4.2 PITN has lower band gap than that of PTh. Polymerization of ITN occurs through 2 and 5 positions of the thiophene ring. Since it is impossible for thiophene and benzene to be aromatic simultaneously, this arrangement induces a competition for aromaticity in the monomer repeat. Due to the high energy of aromatization benzene predicted to remain aromatic and force thiophene to adopt a pseudo-diradical electronic state at the 2 and 5 positions which makes thiophene units to be in the quinoid form and lowers the band gap of the system by decreasing bond length alternation.

Although there are many promising polymer synthesized by the approaches discussed above, during recent years synthesis of donor-acceptor type polymers was proven to be superior compared to the other methods. Donor-Acceptor approach generally divided into two different groups;

The first one is the polymers with acceptor group that directly have resonance interaction on the polymer backbone (with aromatic and quinoid forms) and the second one is the polymers with an acceptor group that inductively modify the polymer backbone.

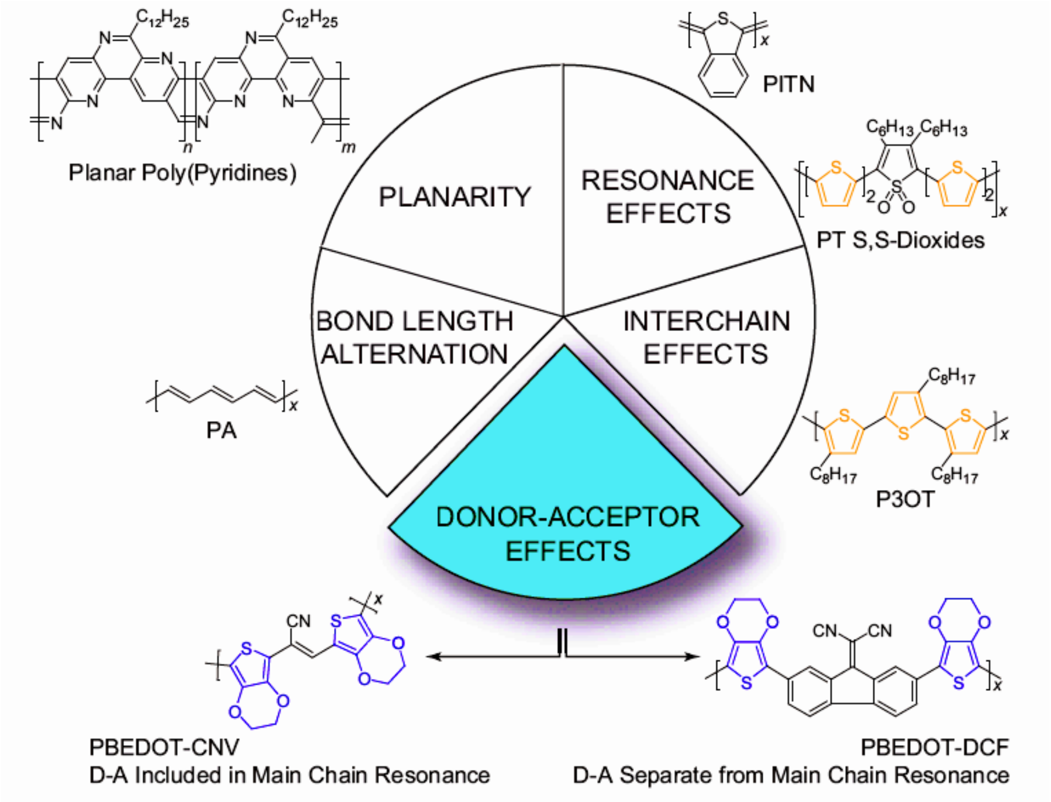


Figure 1. 11 Overview of methods for the modification of band gap.

Due to resonances that enable a stronger double bond character between the donor and acceptor units, donor–acceptor systems lead to a narrower bandgap which in return leads to a decrease in bond length alternation. This is attributed to hybridization between the energy levels, especially the HOMO of the donor and the LUMO of the acceptor (38). The idea is to combine having high HOMO level of the donor and low level of the LUMO of the acceptor in the same polymer to induce a lower band gap. Figure 1.15 illustrates the concept of the donor-acceptor approach (D-A) for PEDOT (39), poly(cyanoacetylene) (PCA) (40) and PBEDOT-CNV. According to D-A theory, the resulting polymer has very similar valence band energy of the donor moiety and has a very close conduction band energy value of the acceptor moiety which makes a tremendously decrease in band gap compared to both PEDOT and PCA.

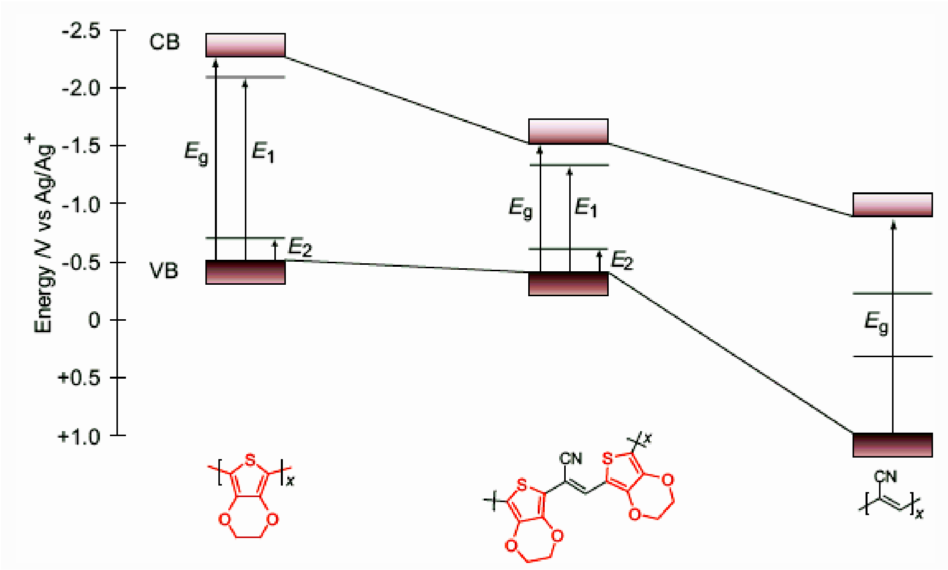


Figure 1. 12 The Donor-Acceptor approach, alternating donor and acceptor moieties results in a polymer that has the combined optical properties of the parent donor or acceptor monomers.

1.10 Selenophene as Donor Group

The search for organic conducting polymers started in the 1970s and up to date largely focused on polyfuran (41), polythiophene (42), polypyrrole (43) and their functional derivatives. Relatively little work was conducted on seleniumcontaining analogues (44). In comparison, the differences in the chemistry of selenium versus sulfur include the increased metallic character and decreased electronegativity of the heteroatom. Hence, selenophene has a lower oxidation potential and higher electron donating character than sulfur analog (45). Lower oxidation potential engenders high quality polymer films during electropolymerization due to minimized harmful effects of high potentials such as degradation of the polymer films as they form (46).

1.11 Pyrrole as Donor Group

Polypyrrole can easily be synthesized chemically or electrochemically and has a wide range of optoelectronic properties available through alkyl and alkoxy substitution which gives it an extensive value as an electrochromic material. The pristine polypyrrole however, has electrochromic properties of low quality. It has a high band gap (2.3 eV). Since it switches between dark colors its optical contrast is low with a moderate switching time in the visible region (47). The number of functionalized polypyrrole derivatives is quite low, (48-54)though numerous studies have been conducted on pristine polypyrrole (55-56).

There are quite low monomers bearing pyrrole as a donor group. In order to improve the pyrrole's fundamental properties and obtain an electroactive monomer possessing superior spectroelectrochemical behaviors pyrrole is a great candidate as a donor group.

1.12 Aim of the Work

Aim of the work is to synthesize new monomers while maintaining acceptor group and varying the donor group. The comparison of the donor groups can be achieved only when keeping other factors constant. The donor-acceptor match has a significant effect on the band gap as discussed before. Increasing the number of electrochromic monomers/polymers helps the variety of colors that are needed for the applications.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

All chemicals were purchased from Aldrich except anhydrous tetrahydrofuran (THF) which was purchased from Acros. 4,7-Dibromobenzo[1,2,5]thiadiazole (57), tert-butyl pyrrole- 1-carboxylate (58), N-(tert-butoxycarbonyl)-2-(trimethylstannyl) pyrrole (58) were synthesized according to previously described methods. Tetrahydrofuran (THF) was distilled over Na/benzophenone prior to use.

2.2 Equipments

2.2.1 Nuclear Magnetic Resonance (NMR) Spectrometer

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Spectrospin Avance DPX-400 Spectrometer and chemical shifts (δ/ ppm) were given relative to tetramethylsilane as the internal standard.

2.2.2 Cyclic Voltammetry (CV) System

Electropolymerization was performed with a Voltalab 50 potentiostat in a three-electrode cell consisting of platinum wire or Indium Tin Oxide (ITO) coated glass as the working electrodes, platinum wire as the counter electrode, and a Ag wire as the pseudo reference electrode. Electrodeposition was performed in a 0.1 M solution of tetrabutylammonium perchlorate (TBAPC) at a scan rate of 100 mV/s for 15 cycles.

2.2.3 UV-Vis-NIR Spectrophotometer

UV–Vis–NIR spectra were recorded on a Varian Cary 5000 spectrophotometer at a scan rate of 2000 nm/min.

2.2.4 Colorimeter

Colorimetry measurements were performed via Minolta CS-100 Spectrophotometer.

2.3 Procedures

2.3.1 Monomer Synthesis

4,7-dibromobenzothiadiazole

To a 500 mL two-necked round bottom flask benzothiadiazole (10.00 g, 73.44 mmol) and 150 mL of HBr (47%) were added. A solution containing Br_2 (35.21 g, 220.32

mmol) in 100 mL of HBr was added dropwise very slowly (slow addition is essential!). After total addition of the Br_2, the solution was refluxed for 6 h. Precipitation of an orange solid was noted. The mixture was allowed to cool to room temperature and sufficient saturated solution of $NaHSO_3$ was added to consume completely any excess Br_2. The mixture was filtered under vacuum and washed exhaustively with water. The solid was then washed once with cold Et_2O and dried under vacuum for ca. 20 h, affording the desired dibrominated product in 95% yield (20.51 g, 69.77 mmol).

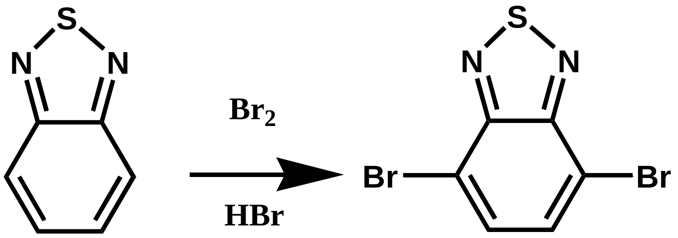


Figure 2. 1 Synthesis of 4, 7-dibromobenzothiadiazole

tert-Butyl Pyrrole-1-carboxylate

Di-*tert*-butyl dicarbonate, $(Boc)_2O$, (7.8 g, 35.7 mmol) and 4-dimethylamino)pyridine, DMAP, (0.5 g, 4.49 mmol) were added to pyrrole (2.0 g, 29.8 mmol) in acetonitrile (30 mL) under argon. After the addition was completed, the mixture was stirred at room temperature for two hours. Evaporation of the solvent and subsequent column chromatography (Al_2O_3, hexane), afforded 4.73 g (95% yield) of tert-butyl pyrrole-1-carboxylate as a colorless liquid.

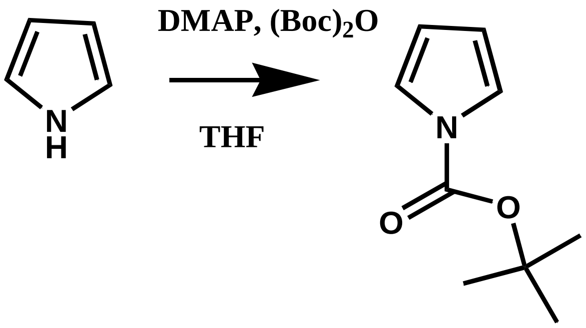


Figure 2. 2 Synthesis of tert-Butyl Pyrrole-1-carboxylate

N-(tert-Butoxycarbonyl)-2-(trimethylstannyl)pyrrole

A 250-mL three-necked flask equipped with magnetic stirrer, a thermometer, a dropping funnel and nitrogen gas inlet was charged with dry THF (40 mL) and 2,2,6,6-tetramethylpiperidine (2.79 g, 19.75 mmol). The mixture was cooled to –78 °C and 18 mL of a 1.6 n solution of *n*BuLi (21.5 mmol) in hexane was added slowly so that the temperature of the mixture always remained below –65 °C. The mixture was stirred for 10 min at –75 °C, then warmed to 0 °C and stirred for additional 10 min. At this point, the mixture was cooled again to –75 °C and a solution of *tert*-butyl pyrrole-1-carboxylate (3 g, 17.94 mmol) in dry THF (40 mL) was added while keeping the temperature below –65 °C. The mixture was stirred for additional 90 min while keeping the temperature below –65 °C. A solution of Bu_3SnCl (7.5 mL, 23.32 mmol) in dry THF (40 mL) was added dropwise to the reaction mixture while keeping the temperature below –65 °C. The reaction was stirred for 40 min at –75 °C and for additional 40 min at 0 °C and then for 12 h at room temperature. After removal of the THF under reduced pressure, water (50 mL) and diethyl ether (50 mL) were added to the crude and the aqueous phase was extracted with three portions of diethyl ether. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. Column chromatography (Al_2O_3, hexane) of the resulting oil afforded 6.18 g (75% yield) of the product as a yellow liquid.

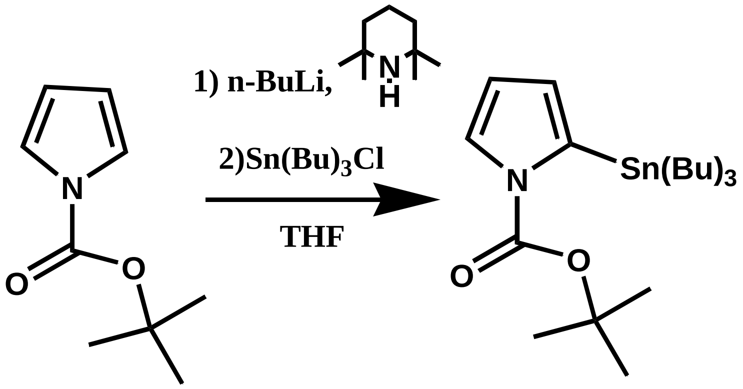


Figure 2. 3 Synthesis of N-(tert-Butoxycarbonyl)-2-(trimethylstannyl)pyrrole

4,7-Di(N-(tert-butoxycarbonyl)-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole

4,7-Dibromobenzothiadiazole (294 mg, 1.0 mmol), and N-(tert-butoxycarbonyl)-2-(tributylstannyl) pyrrole (2.29 g, 5.0 mmol) were dissolved in anhydrous THF (150 ml) and purged with argon for 30 min. Then, dichlorobis(triphenyl phosphine)-palladium(II) (75 mg, 0.068 mmol) was added at room temperature under argon atmosphere. The mixture was refluxed for 3 days. Solvent was evaporated under vacuum and the crude product was purified by column chromatography on neutral alumina (eluent DCM:hexane, 1:1 v/v) to obtain 463 mg (63%) of 4,7-di(N-(tert-butoxycarbonyl)-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole.

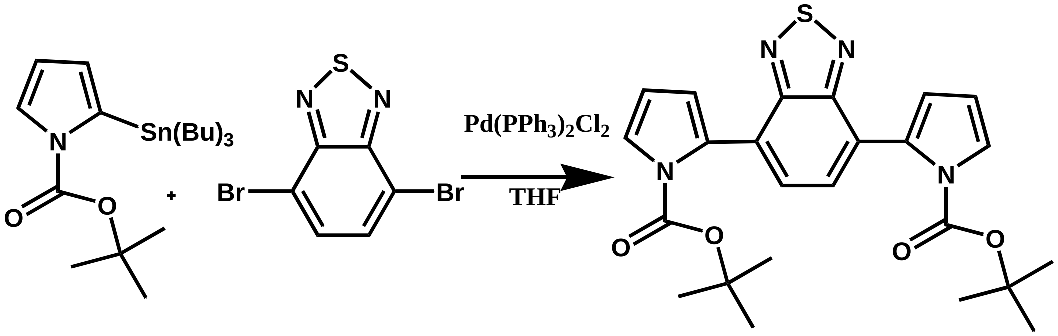


Figure 2. 4 Synthesis of 4,7-Di(N-(tert-butoxycarbonyl)-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole

4,7-Di(1H-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole (PYBTPY)

4,7-Di(N-(tert-butoxycarbonyl)-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole (127 mg, 0.48 mmol) was dissolved in 60 ml methanol. 120 mg Na, (5.2 mmol) were added and the reaction mixture was heated under reflux for 24 h. The solvent was evaporated and the residue was treated with water and extracted with dichloromethane. The organic extracts were dried over $MgSO_4$, the solvent was evaporated and the residue chromatographed on a column with silica gel using hexane:DCM (4:1 v/v) as eluent 92 mg (72%) PYBTPY was isolated.

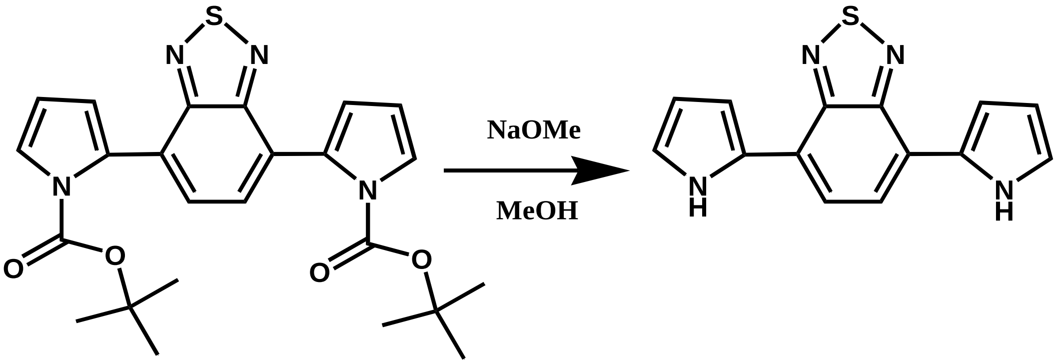


Figure 2. 5 Synthesis of4,7-Di(1H-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole (PYBTPY)

Tributyl(2-selenophenyl)stannane

Stanylation of selenophene was achieved in one step according to a previously reported method (46). Selenophene (1 g, 7.64 mmol) was dissolved in anhydrous THF (10 ml) in argon atmosphere. Solution was cooled to -30 ^{0}C in orthoxylene - liquid nitrogen bath and subsequently n-butyllithium (1.76 ml of 2.0 M solution in hexane, 3.52 mmol) was added dropwise. Mixture was stirred at this temperature for 3.5 hours. Tributyltin chloride (1.3 g, 4 mmol) was added dropwise and stirred for another hour at this temperature. 20 ml of dichloromethane were added and the solution was extracted three times with saturated aqueous sodium carbonate. Organic phase was extracted two times with brine solution. The organic extract was dried over MgSO4 and the solvent evaporated under reduced pressure. The residue was further purified by neutral alumina with petroleum ether as eluent to yield colorless oil (0.72g, 45%).

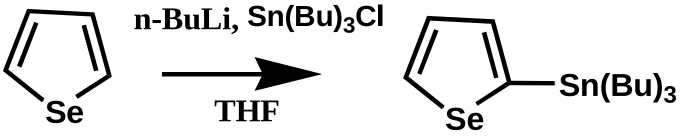


Figure 2. 6 Synthesis of tributyl(2-selenophenyl)stannane

4,7-Di(2-selenophenyl)benzo[c][1,2,5]thiadiazole (SeBTSe)

4,7-Dibromobenzothiadiazole (294 mg, 1.0 mmol)and tributyl(2-selenophenyl)stannane(1.68 g, 4mmol) were dissolved in anhydrous THF (100ml), the solution was purged with argon for 30 min. And dichlorobis(triphenyl phosphine)-palladium(II) (50 mg, 0.045 mmol) was added at room temperature under argon atmosphere. The mixture was refluxed for 18 hours under argon atmosphere. Solvent was evaporated under vacuum and the crude product was purified by column chromatography on a SiO2 column to obtain 4,7-di(2-selenophenyl)benzo[c][1,2,5]thiadiazole

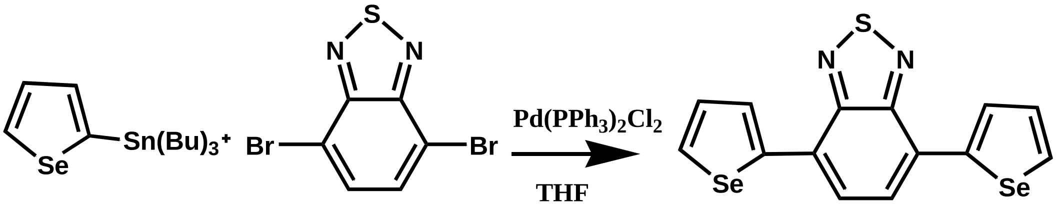


Figure 2. 7 Synthesis of 4,7-Di(2-selenophenyl)benzo[c][1,2,5]thiadiazole (SeBTSe)

2.3.2 Synthesis of Polymers

The potentiodynamic electropolymerization of monomer on ITO was performed in a 0.1 M TBAPC and 1x10^{-2} M PYBTPY and SEBTSE solutions via applying potentials between 0.0 V and +1.0 V at a scan rate of 100 mV/s by multiple scan voltammetry. Due to the poor solubility of the monomer in acetonitrile (ACN), a mixture of ACN and dichloromethane (DCM) (95/5, v/v) was chosen as the solvent. The free standing homopolymers were washed with ACN in order to remove TBAPC and unreacted monomer after the electrolysis.

2.4 Characterization of Polymer Films

2.4.1 Cyclic Voltammetry

The power of electrochemical methods that can be applied to the study of conducting polymer films deposited on a conducting surface is fairly broad and it has been thoroughly reviewed by Doblhofer et al. Among these methods, cyclic voltammetry (CV) has becoming increasingly popular as a mean to study redox states, due to its simplicity and versatility. Using CV, the electrode potential at which a polymer undergoes reduction or oxidation can be rapidly located, information regarding the stability of the product during multiple redox cycles can be revealed. Since the rate of potential scan is variable, both fast and slow reactions can be followed. During a single experiment, CV has the ability to generate a new redox species at the first potential scan and then investigate the characteristic behaviors of species on the second and subsequent scans.

CV consists of linearly scanning the potential of a stationary working electrode using a triangular potential waveform (Figure 2.8. (a)). During the potential sweep, the potentiostat measures the current resulting from the applied potential. A typical CV investigation generally starts at low potentials where no redox reactions occur in anodic direction. After the electrode has reached sufficient potentials at which the monomer starts to get oxidized to a radical cation, anodic current starts to increase until the concentration of the monomer at the electrode surface approaches zero, which is signified by the formation of a peak. The intensity of the current starts to decay since the solution in the vicinity of the electrode has almost zero monomer concentration. The reduction of the deposited polymer is observed in the cathodic run. Upon consecutive cycling, a new oxidation peak appears due to the polymer. Due to increase in the active area of the working electrode owing to coating of an electroactive polymer on a metal electrode, there is an increase in the intensity of the current as the number of cycles increases. (Figure 2.8. (b))

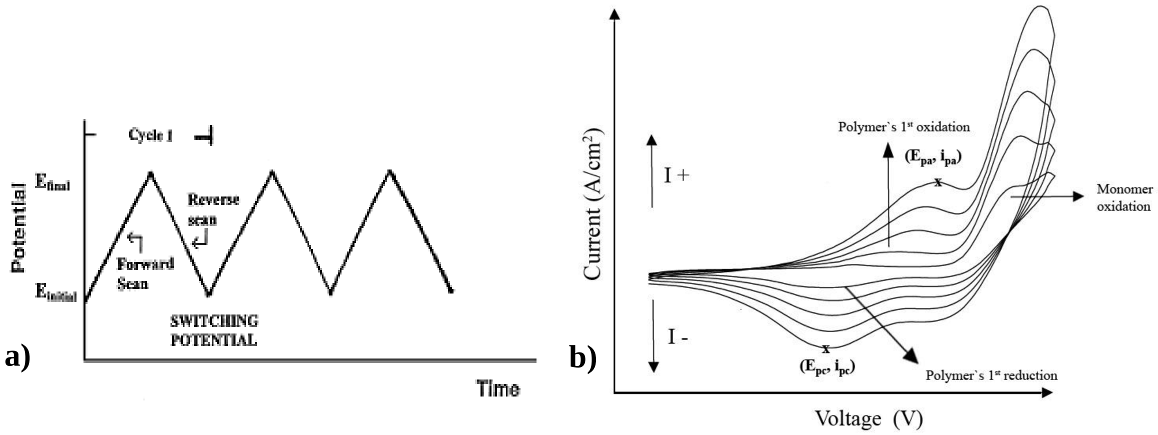


Figure 2. 8 a) Typical Potential−Time excitation signal in CV b) CV of a representative type of electroactive monomer.

The Randles-Sevcik equation states that the peak current is given by:

$$i_p = (2.69 \text{ x } 10^5)n^{3/2}ACD^{1/2}\,V^{1/2}$$

where n is the number of electrons, A is the surface area of the electrode (cm^2), D is the diffusion constant (cm^2/s), C is the bulk concentration of electroactive species (mol/cm^3), and V is the scan rate (V/s). Therefore, for diffusion controlled system, the peak current is proportional to the square root of the scan rate. The rules change in electroactive polymer electrochemistry, when the polymer is adhered to the electrode surface. Hense, the process is not diffusion controlled, and cannot be described by the Randles-Sevcik equation discussed above. Instead, the peak current for a surface bound species is given by the following equation:

$$i_p = n^2F^2\Gamma\ V / 4RT$$

where Γ is the concentration of surface bound electroactive centers (mol/cm^2) and F is Faradays constant (96,485 C/mol). Thus, if a species is surface bound, both the anodic and cathodic peak current will scale linearly with scan rate. In a scan rate dependence experiment, the electroactive polymer is washed and placed in monomer-free electrolyte solution, and the polymer is then cycled between its oxidized and reduced forms at various scan rates while the i_p of both oxidation and reduction is monitored. If the i_p scales linearly with scan rate, then the process is said to be non-diffusion controlled, and the electroactive centers of the polymer are adhered to the electrode surface.

2.4.2 Spectroelectrochemistry

Spectroelectrochemistry is a combination of electrochemical and spectroscopic techniques that can be operated at the same time. Compared to common electrochemical methods, it can provide information on both electrochemical response and accompanying optical characteristics of all states of the electrochemical reaction. It is essential to gather information in-situ during electrochemical process. For the spectroelectrochemical studies, the polymer film coated ITO is placed in a cuvette that is equipped with a reference electrode and a Pt wire counter electrode. This cell is then connected to a potentiostat. The redox switching of conjugated polymers is accompanied by changes in electronic transitions. These electronic transitions can be probed with the use of UV-Vis spectroscopy. The polymer is stepwise oxidized while obtaining a spectrum at each potential. The results are then recorded as a graph of the extent of absorption as a function of wavelength. Spectroelectrochemistry experiments reveal key properties of conjugated polymers such as band gap (E_g), λ_{max}, the intergap states that appear upon doping and the evolution of polaron and bipolaron bands.

2.4.3 Switching Properties

For electrochromic applications, the significant point is the ability of a polymer to switch rapidly and exhibit a striking color change. Electrochromic switching studies can monitor absorbance changes with time during repeated potential stepping between bleached and colored states to obtain an insight into changes in the optical contrast (Figure 2.9). A square wave potential step method coupled with optical spectroscopy known as chronoabsorptometry is used to probe switching times and contrast in these polymers. Switching time is a time required for the polymer film to step between its oxidized and reduced states. In this study the potential is set at an initial value for a set period of time and is then stepped to a second potential for a set period of time before being switched back to the initial potential. Electrochromic contrast is often reported as percent transmittance change (ΔT %) at a specified wavelength where the material has the highest optical contrast.

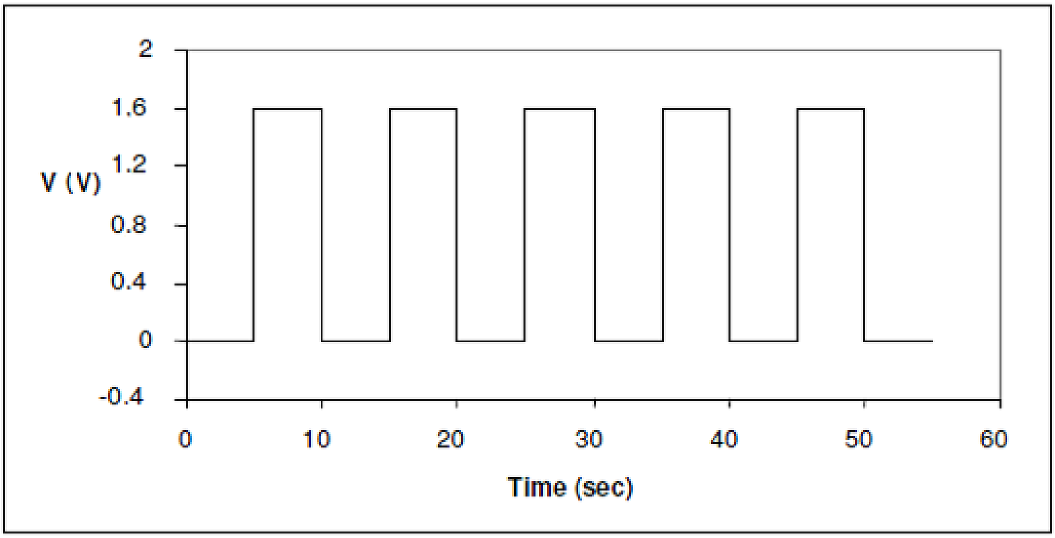


Figure 2. 9 Square wave voltammetry

2.4.4 Colorimetry

Colorimetry provides scientific means to define color. Rather than measuring the absorption bands, colorimetry measures the human eye's sensitivity to light across the visible region and graphically representing the track of doping-induced color changes of an electrochromic material or device. A commonly used scale that numerically defines colors has been established in 1931 by The Commission Internationale de l'Eclairge (CIE system) with L*a*b, CIE color spaces (Figure 2.10). Color measurements were performed via Coloreye XTH Spectrophotometer. This technique measures three values in relation to color: the hue (dominant wavelength), which is the wavelength where maximum contrast occurs, saturation (purity), which is the color’s intensity, and brightness (luminance).

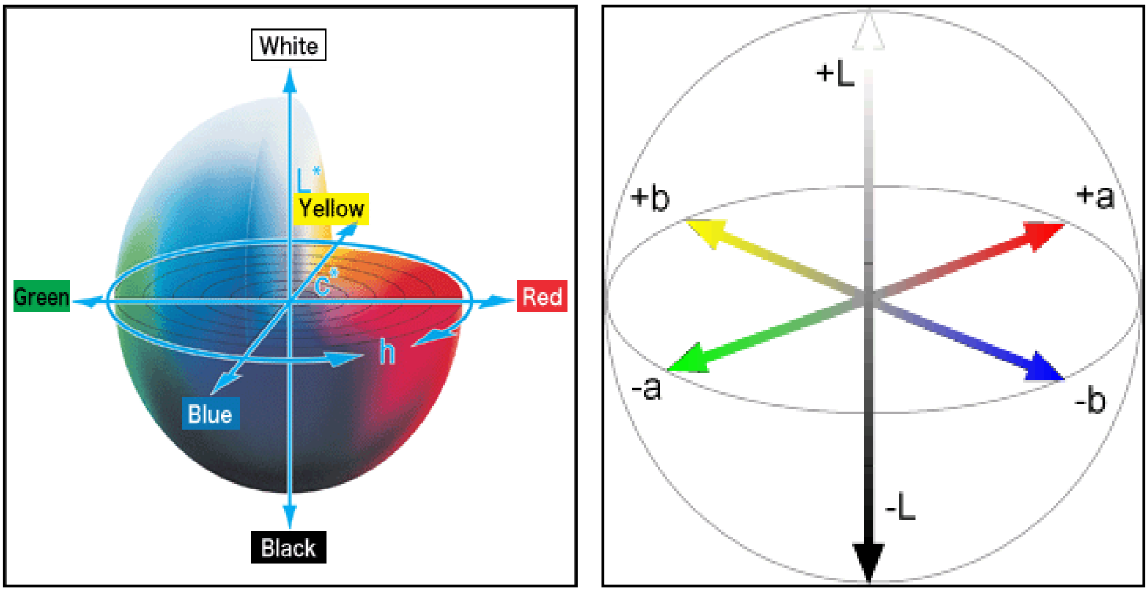


Figure 2. 10 CIELAB color space

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Characterization of the D-A-D Molecules

^{1}H-NMR, ^{13}C-NMR spectra of monomers were investigated in $CDCl_3$ and chemical shifts (δ) were given relative to tetramethylsilane as the internal standard. Mass analyses were also performed for the characterization of monomers.

3.1.1 4,7-Di(1H-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole

^{1}H NMR ($CDCl_3$, δ): 6.25 (dd J=0.45 and 1.48 Hz , Hb), 6.80 (dd, J=0.11 and 0.45 Hz ,Hc), 6.95 (dd, J= 0.11 and 1.48 Hz, Ha), 7.79 (s, 2H,), 10.82 (s, 2H). ^{13}C NMR ($CDCl_3$, δ): 106.0 ; 108.9 ; 118.9 ; 120.3 ; 122.2 ; 128.4 ; 151.2

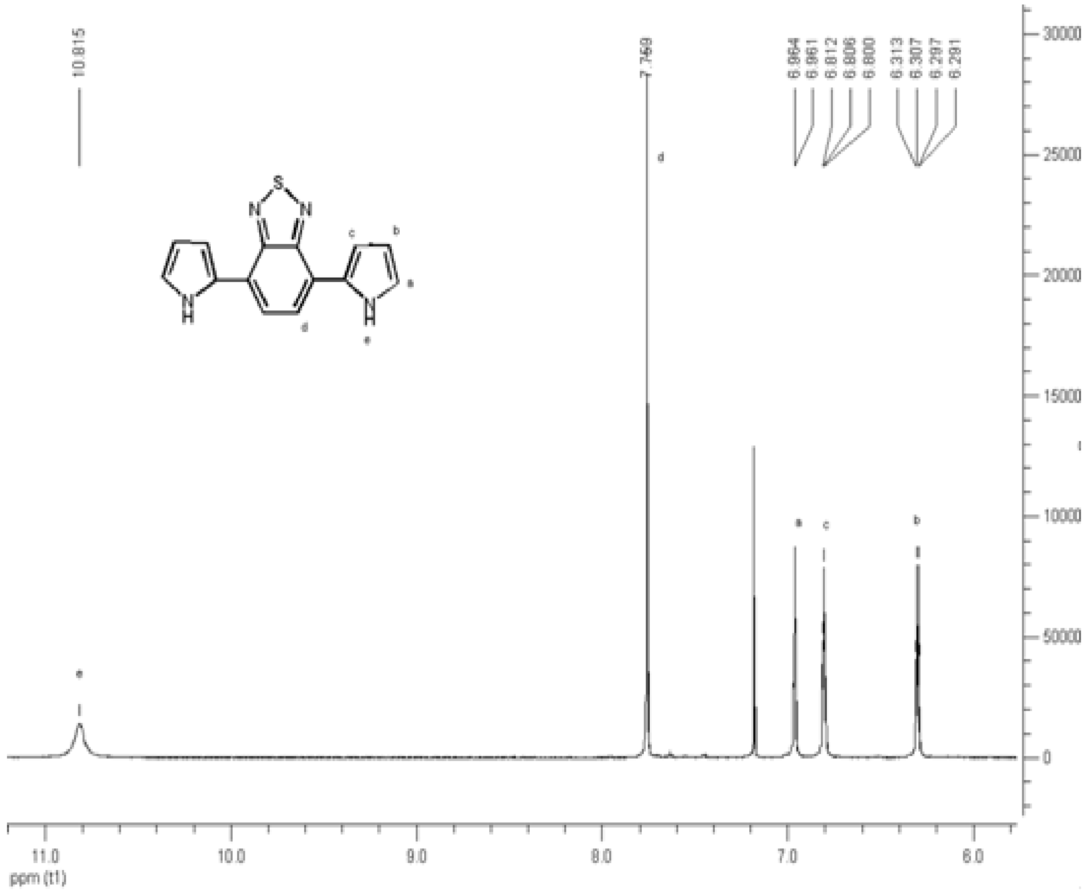


Figure 3. 1 ^{1}H-NMR spectrum of PYBTPY

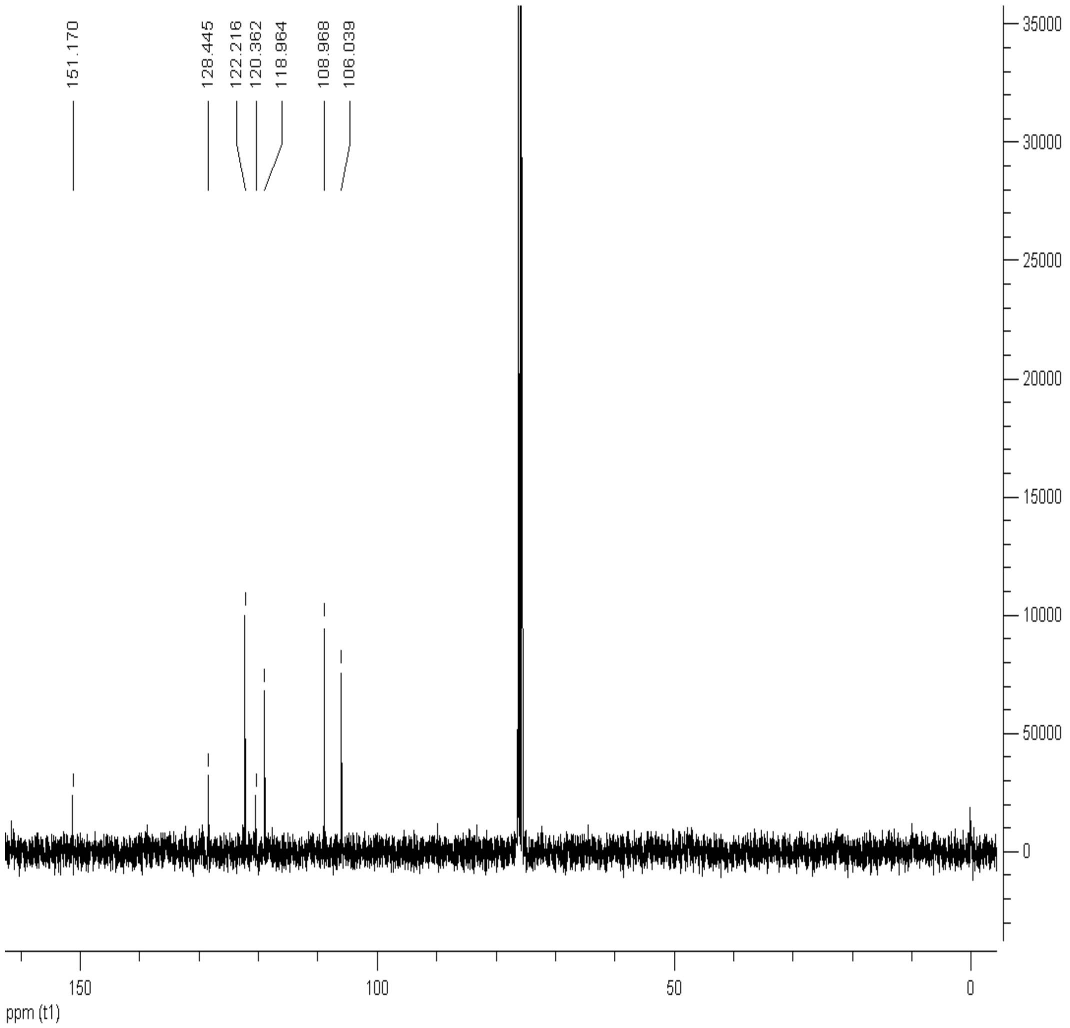


Figure 3. 2 ^{13}C-NMR spectrum of PYBTPY

3.1.2 4, 7-Di(2-selenophenyl)benzo[c][1,2,5]thiadiazole

^{1}H NMR ($CDCl_3$, δ): 7.10 (dd J=3.73 and 5.04Hz, Hb), 7.30 (dd J=0.95 and 5.06Hz, Hc), 7.75 (s, 2H,), 8.05 (dd J=0.95 and 3.63 Hz, Ha). ^{13}C NMR ($CDCl_3$, δ): 124.0; 124.2 ; 125.0 ; 125.8 ; 126.2 ; 137.4 ; 150.2

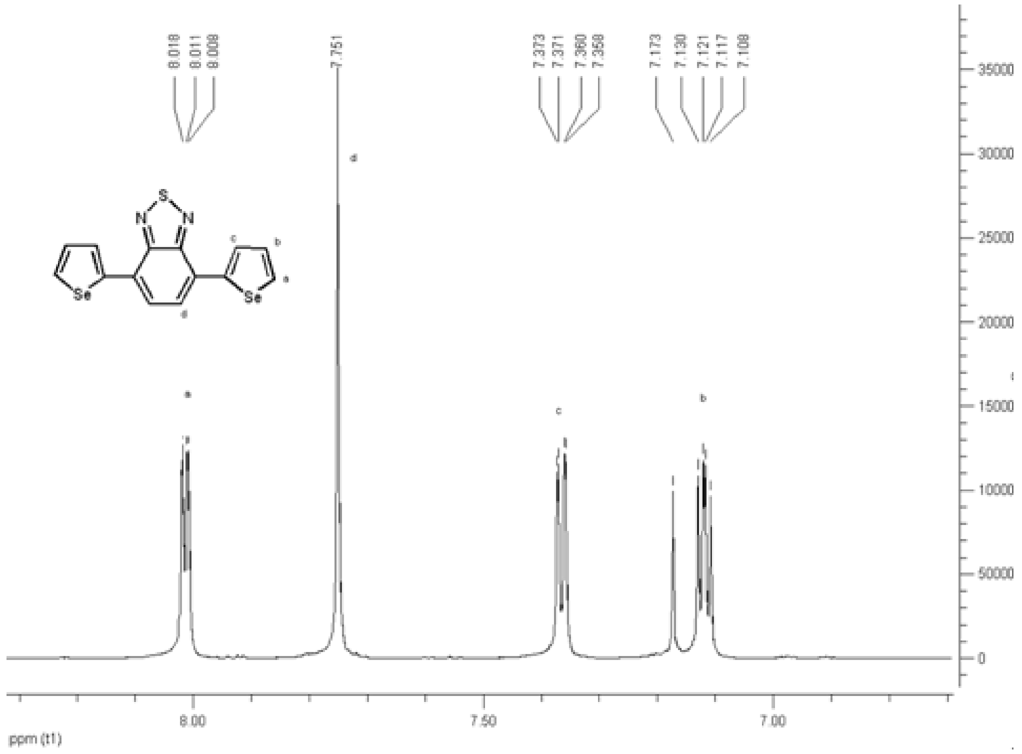


Figure 3. 3 ^{1}H-NMR spectrum of SEBTSE

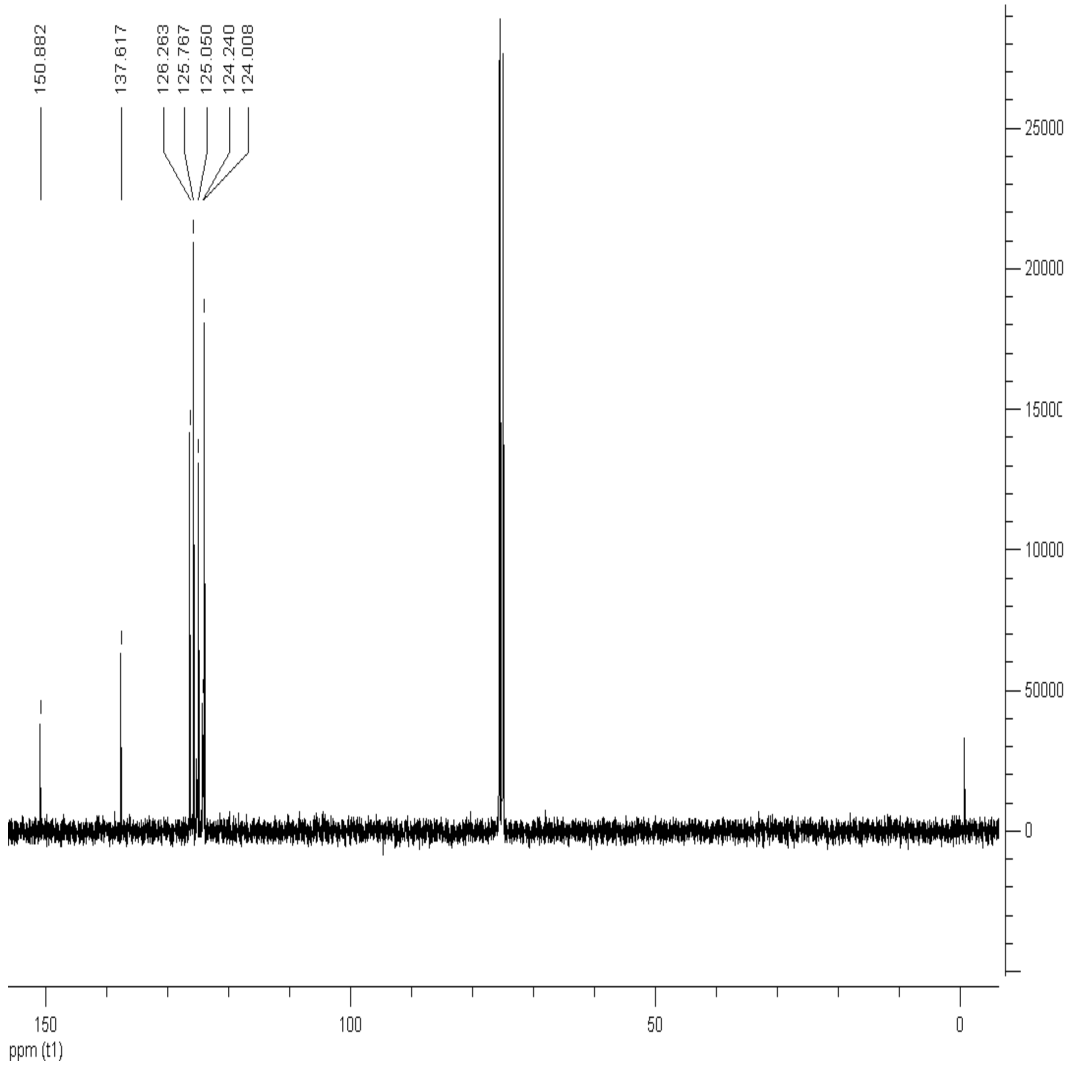


Figure 3. 4 ^{13}C-NMR spectrum of SEBTSE

3.2 Electrochemical and Electrochromic Properties of Donor-Acceptor-Donor Type Polymers

3.2.1 Electrochemical and Electrochromic Properties of Poly(4,7-di(1H-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole P(PYBTPY) and Poly(4,7-di(selenophen-2-yl)benzo[c][1,2,5]thiadiazole P(SEBTSE)

Electrochemistry of Monomers

The potentiodynamic electropolymerization of monomer on ITO was performed in a 0.1 M tetrabutylammonium perchlorate (TBAPC) and $1x10^{-2}$ M PYBTPY solution applying potentials between -0.3 V and +0.7 V at a scan rate of 100 mV/s via multiple scan voltammetry. Some other electrolytes such as tetrabutylammonium tetrafluoroborate and tetrabutylammonium hexafluorophosphate were not as good as this one in terms of polymer film formation on electrodes. Due to the poor solubility of the monomers in acetonitrile (ACN), a mixture of ACN and dichloromethane (DCM) (95/5, v/v) was chosen as the solvent.

The representative electrochemical growth revealing electroactivity of monomers PYBTPY and SEBTSE as well as formation of corresponding insoluble polymers are given in Figures 3.7 and 3.8 respectively.

The monomer (PYBTPY) oxidation potential was observed at 0.65 V (Figure 3.5), which is quite lower than the oxidation potential of pyrrole. After the first cycle, an oxidation peak at 0.2 V and its reverse cathodic peak at 0.15 V appeared. These values are also quite lower than those for polypyrrole.

On the other hand, the monomer (SEBTSE) has an oxidation potential of 1.2 V (Figure 3.6), which is also lower than the oxidation potential of polyselenophene

(59). This proves that the acceptor group lowers the oxidation potentials of both monomers. This observation can be attributed to effective Donor–Acceptor match.

After subsequent runs electroactivity increases with increasing scan number. The peak at 0.65 V decreases as a result of monomer consumption in the diffusion layer. PYBTPY was coated on Pt wire potentiodynamically over 40 cycles from a 0.01 M monomer and 0.1 M TBAPC DCM/ACN (5/95, v/v) solution. Anodic and cathodic peak currents revealed a linear relationship as a function of scan rate for polymer film, indicating that electrochemical processes are not diffusion limited and reversible even at high scan rates (60) (61).

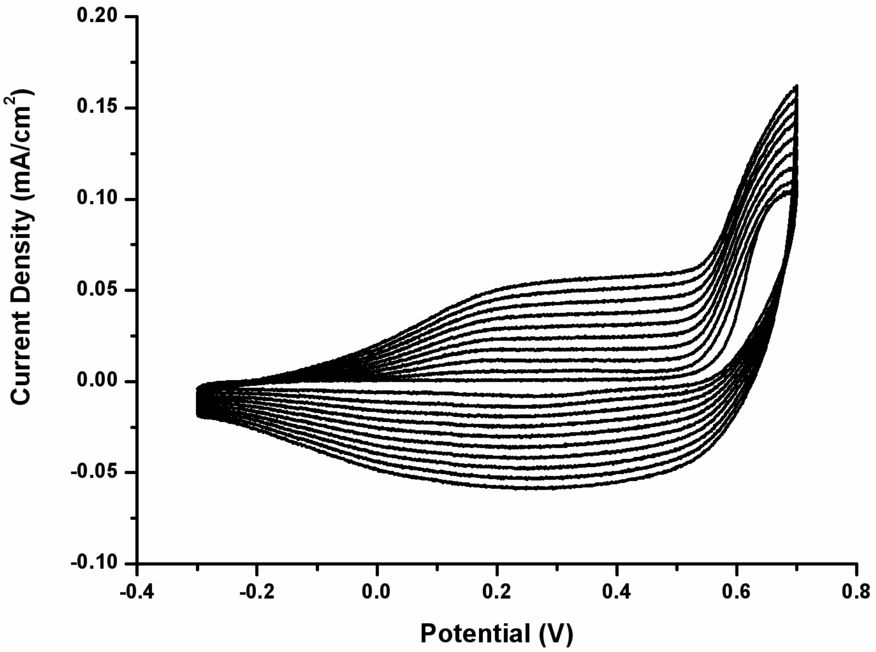


Figure 3. 5 Repeated potential scan electropolymerization of PYBTPY (10^{-2} M) at 100 mV/s in 0.1 M TBAPC in DCM/ACN (5/95, v/v) on ITO electrode vs Ag wire after 40 cycles

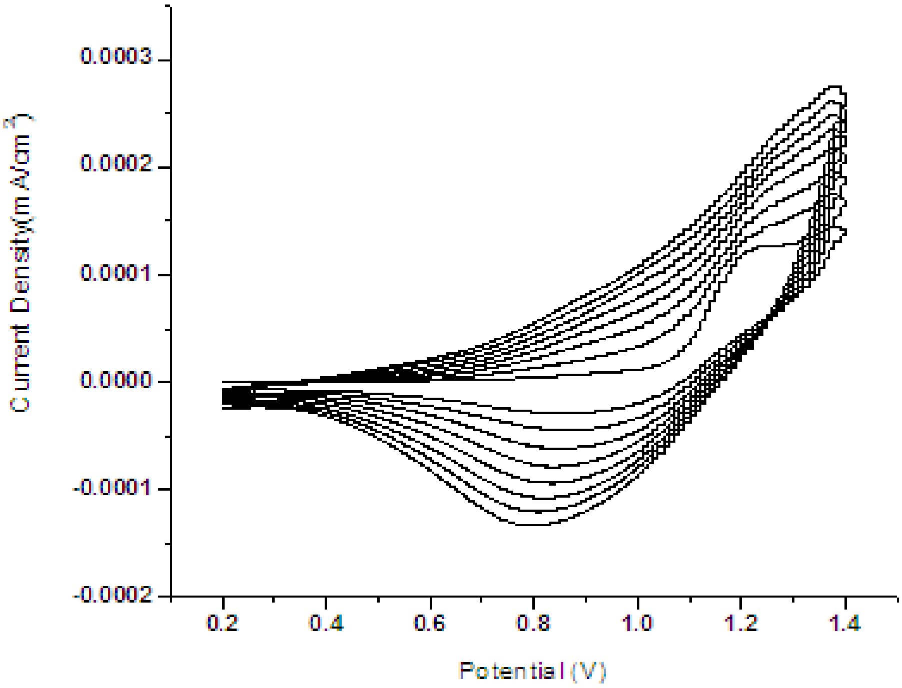


Figure 3. 6 Repeated potential scan electropolymerization of PSEBTSE (10^{-2} M) at 100 mV/s in 0.1 M TBAPC in DCM/ACN (5/95, v/v) on ITO electrode vs Ag wire after 40 cycles

A direct relation between current response and scan rate was observed for polymer film which proved that the film was well adhered on the electrode surface and electroactive (Figure 3.7 and 3.8).

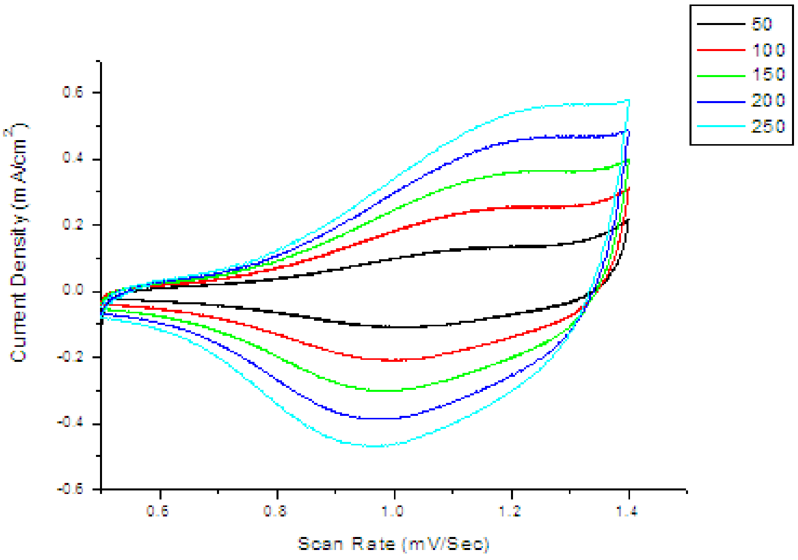


Figure 3. 7 Scan rate dependence of PSEBTSE film on Pt vs Ag wire in 0.1 M TBAPC/ACN (a) 50, (b) 100, (c) 150, (d) 200, (e) 250 mV/s

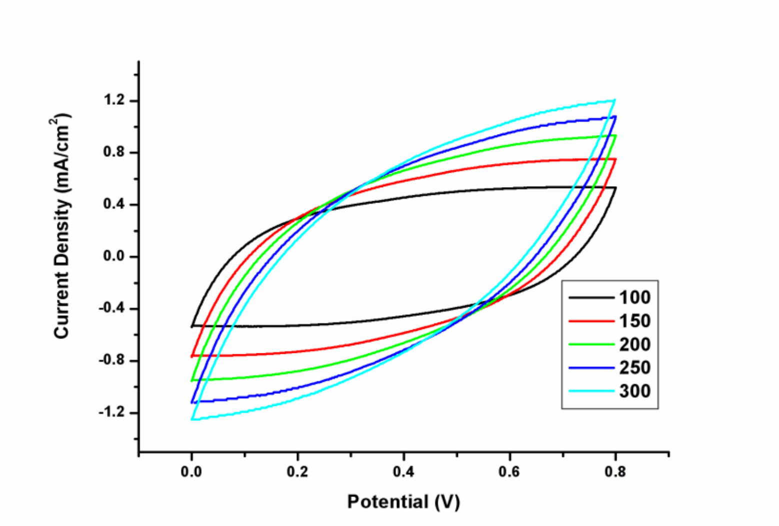


Figure 3. 8 Scan rate dependence of PPYBTPY film on Pt vs Ag wire in 0.1 M TBAPC/ACN (a) 100, (b) 150, (c) 200, (d) 250, (e) 300 mV/s

Spectroelectrochemistry of Poly(4,7-di(1H-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole P(PYBTPY)

Spectroelectrochemical studies were performed in order to monitor in situ optical changes upon doping. Spectral changes were recorded by UV–Vis–NIR spectrophotometer in a monomer free, 0.1 M TBAPC/ACN solution while varying the applied potential between -0.3 V and +1.0 V. Generally, donor acceptor type polymers show two distinct absorption maxima due to high energy and low energy π-π* transitions (62). As a donor acceptor polymer, PPYBTPY showed these absorption maxima due to the transitions from pyrrole based valence band to its antibonding counterpart as well as to the substituent localization narrow conduction band (63).

As doping proceeds, formation of charge carriers leads to new absorption bands at 710 nm and 1200 nm while absorbtions for the neutral state are decreasing. This change represents the formation of polaron and bipolaron bands respectively (64).

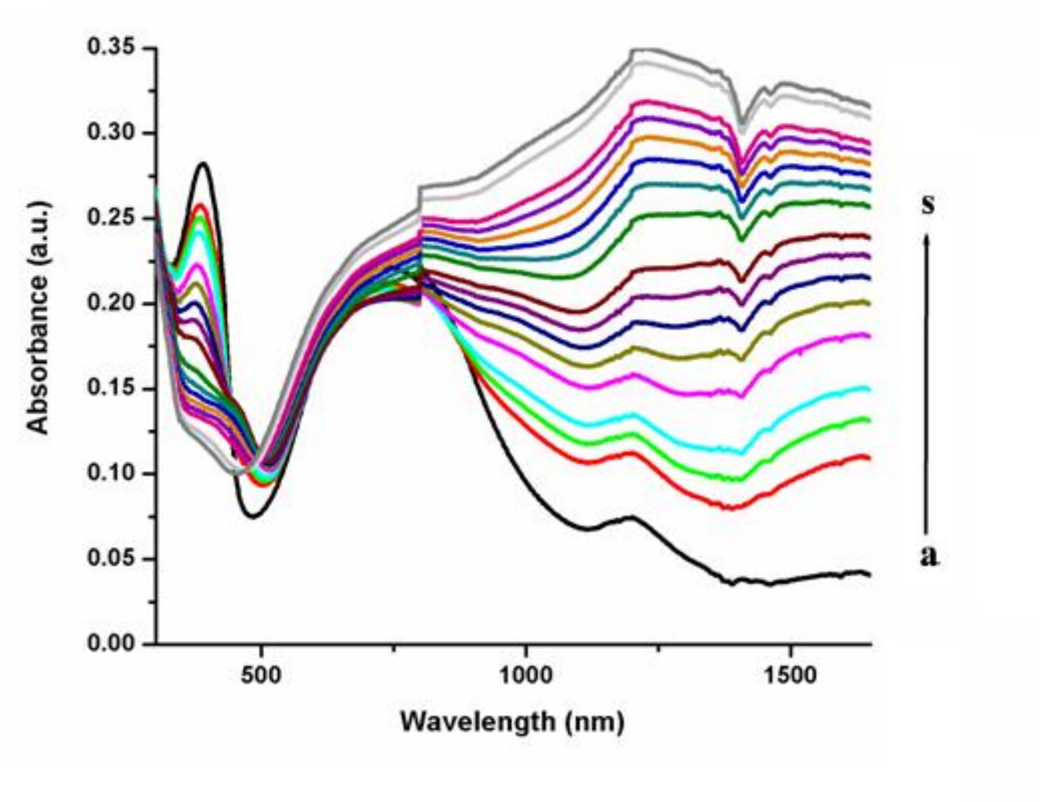
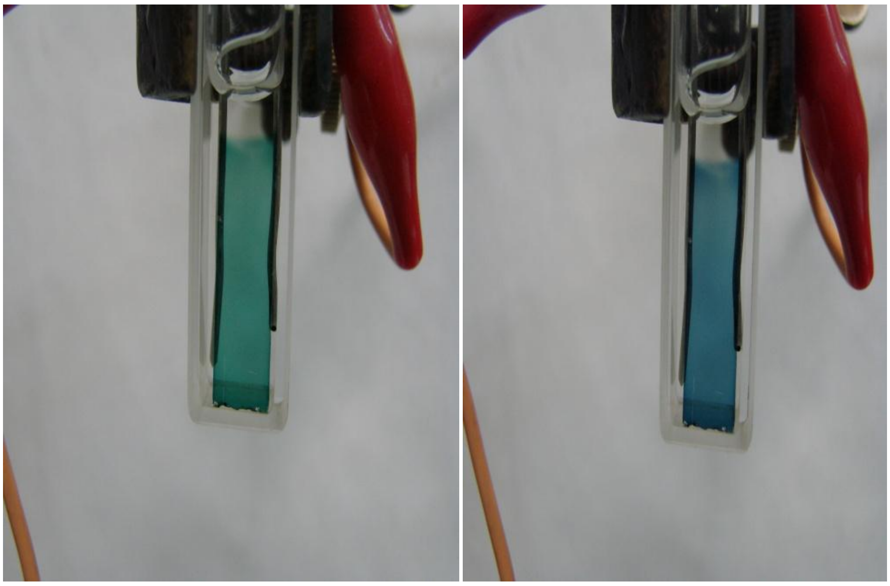


Figure 3. 9 Spectroelectrochemistry of PPYBTPY film on ITO-coated glass slide in a monomer free, 0.1 M TBAPC/ACN electrolyte–solvent couple at applied potentials (V) vs Ag wire: (a)-0.3, (b) 0, (c) 0.05, (d) 0.1, (e) 0.15, (f) 0.2, (g) 0.25, (h) 0.3, (i) 0.35, (j) 0.4, (k) 0.5, (l) 0.55, (m) 0.6, (n) 0.65, (o) 0.7, (p) 0.8, (q) 0.85, (r) 0.9, (s) 0.1



(a) (b)

Figure 3. 10 Colors of PPyBTPy (a) neutral and (b) oxidized state

The band gap of the PPYBTPY is 1.13 eV which was calculated from the onset of the second π-π* transition. Spectroelectrochemical studies for the polymer film showed that the color of the film changed from saturated green (Y:464, x:0.301, y:0.401) to brownish green (Y:492, x:0.309, y:0.358) during oxidation (Figure 3.10). Coloration efficiency is the ratio between the injected/ejected change per unit area of the electrode and the change in the optical density at a dominant wavelength. Coloration efficiency of the PPYBTPY was found to be 85 cm^2 C^{-1} at 100% full switch at 390 nm.

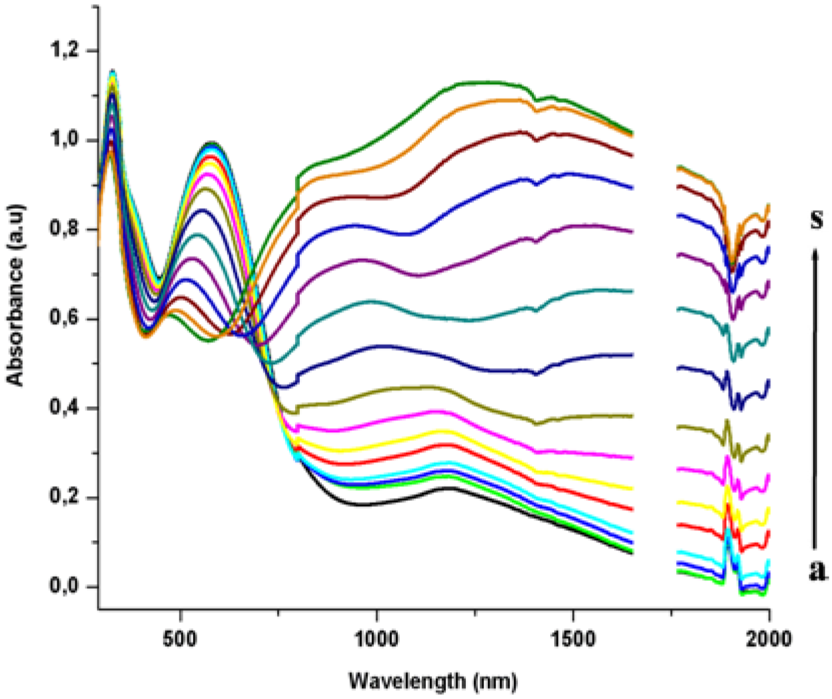


Figure 3. 11 Spectroelectrochemistry of PSEBTSE film on ITO-coated glass slide in a monomer free, 0.1 M TBAPC/ACN electrolyte–solvent couple at applied potentials (V) vs Ag wire: (a)-0.3, (b) 0, (c) 0.05, (d) 0.1, (e) 0.15, (f) 0.2, (g) 0.25, (h) 0.3, (i) 0.35, (j) 0.4, (k) 0.5, (l) 0.55, (m) 0.6, (n) 0.65, (o) 0.7, (p) 0.8, (q) 0.85, (r) 0.9, (s) 0.1

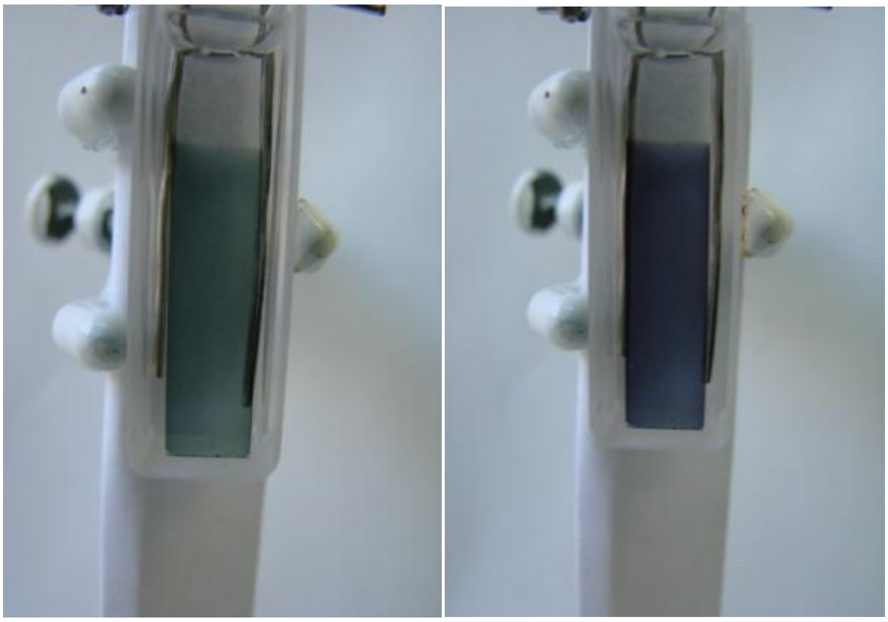


Figure 3. 12 Colors of PSeBTSe (a) neutral and (b) oxidized state

The spectroelectrochemical series for PSeBTSe is shown in Figure 3.11. In visible region the polymer exhibits only one transition from the valence band to conduction band (π-π*). Spectroelectrochemical studies for the polymer film showed that the color of the film changed from saturated brownish green (Y:496, x:0.389, y:0.313) to dark blue (Y:511, x:0.397, y:0.388) during oxidation (Figure 3.12). The band gap energy measured as the onset of the π-π* absorption was calculated for PSEBTSE. The wavelength at which polymer shows π-π* transition is defined as the maximum wavelength (λmax). Using de Broglie equation, the band gap (Eg) is found as 1.42 eV at 580 nm for PSEBTSE.

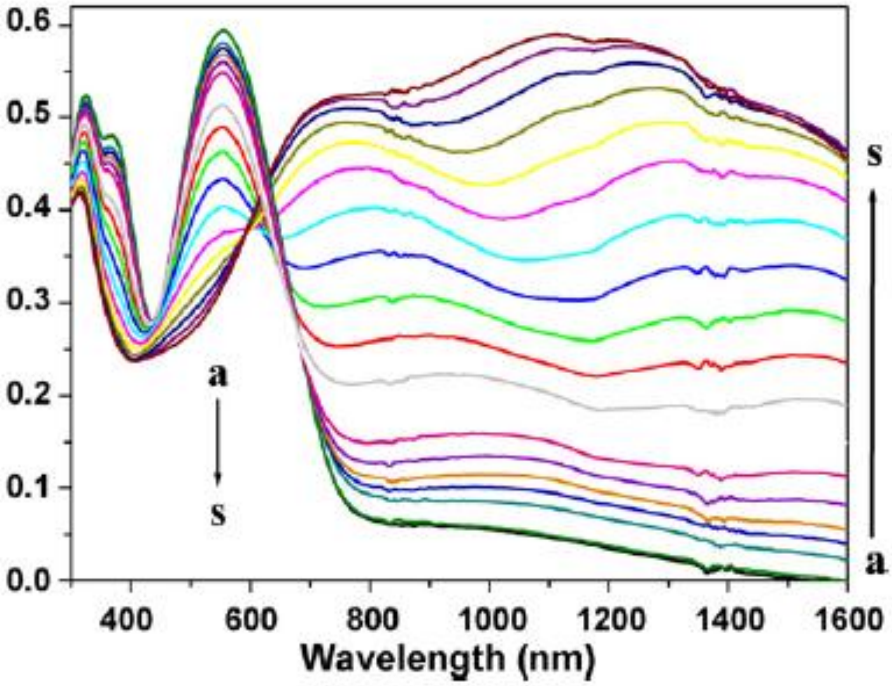


Figure 3. 13 Spectroelectrochemistry of PSBTS film on ITO-coated glass (a)−0.90V, (b)−0.1V, (c) 0.35V, (d) 0.4V, (e) 0.45V, (f) 0.50V, (g) 0.55V, (h) 0.60V, (i) 0.65V, (j) 0.70V, (k) 0.75V, (l) 0.80V, (m) 0.85V, (n) 0.90V, (o) 0.95V, (p) 1.00V, (q) 1.05V, (r) 1.10V, (s) 1.15V

According to the study of Atwani. (65) on poly(4,7-dithien-2-yl-2,1,3-benzothiadiazole) the spectroelectrochemical series for PSBtS is shown in Figure 3.11 . In this case, the absorbance of the π-π* transition in the neutral state (−0.90 V) is displaying a maximum at 560 nm. The electronic band gap according to the π-π* transition is published as 1.5 eV (65).

Since, electron donation is a cause which effects the band gap according to the donor-acceptor theory, band gaps of these three monomers give information about the donation ability of the donor groups. Upon comparing the donor molecules, selenophene and thiophene show almost same properties with respect to their band gaps (1.43eV and 1.50eV respectively). On the other hand, pyrrole is much more donating than selenophene and thiophene hence, it decreases the band gap (1.13eV).

Electrochromic switching of

Poly(4,7-di(1H-pyrrol-2-yl)benzo[c][1,2,5]thiadiazole) P(PYBTPY)

In order to determine switching time and percent transmittance change (ΔT%) for the polymers they were polymerized on ITO coated glass slides. Applied potentials were stepped between -0.3 V and 1.0 V with a switching interval of 5 s in 0.1 M TBAPC/ACN while recording percent transmittance as a function of time

PPYBTPY film showed 37 % optical contrast at 390 nm and 71 % optical contrast at 1230 nm. A square-wave potential step method was used to calculate switching time. The polymer achieved 95 % of its optical contrast in 0.9 s at 390 nm. At 1230 nm, switching time waas recorded as 1.3 s. (Figure 3.14 and 3.15).

The optical contrast for PSEBTSE was measured as 24 % at 580 nm and 71 % at 1300 nm with a switching time of 1.1 and 0.9 sec respectively. In the NIR region they both showed remarkable contrasts of 71 % which confirmed that they can be used for near-IR applications. (Figure 3.16 and 3.17).

Kinetic studies for polymer films showed that polymers have not only high optical contrast but also fast switching times.

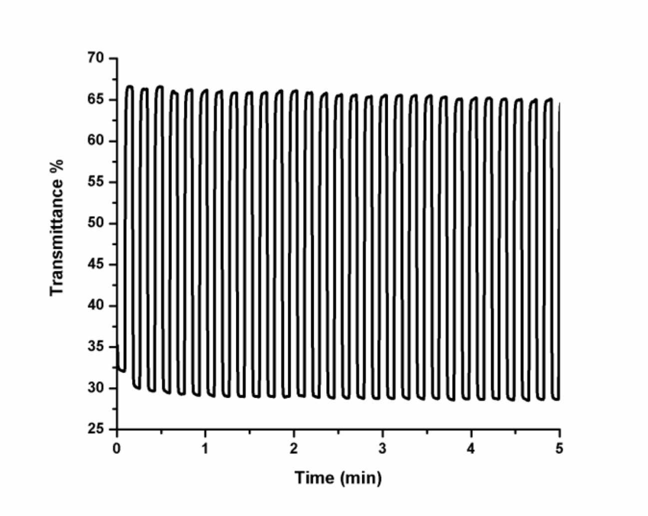


Figure 3. 14 Electrochromic switching, percent transmittance change monitored at 390 nm for PPYBTPY in 0.1 M TBAPC/ACN

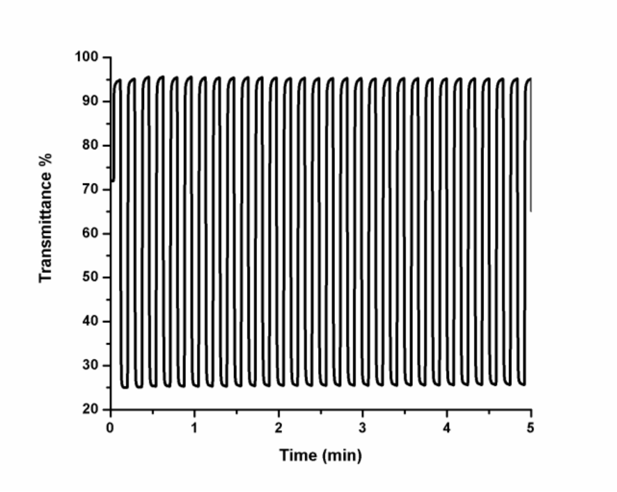


Figure 3. 15 Electrochromic switching, percent transmittance change monitored at 1230 nm for PPYBTPY in 0.1 M TBAPC/ACN

PPYBTPY	**390 nm**	**1230 nm**
Optical contrast	**37 %**	**71 %**
Switching time	**0.9 sec**	**1.3 sec**

Table 3. 1 Optical contrasts and related switching times of PPYBTPY

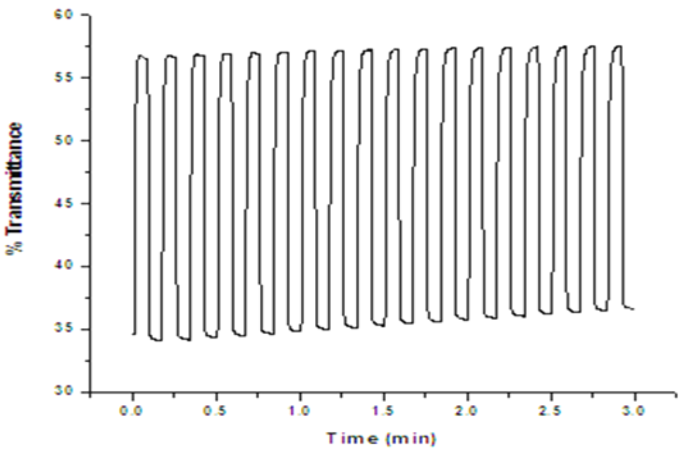


Figure 3. 16 Electrochromic switching, percent transmittance change monitored at 580 nm for SEBTSE in 0.1 M TBAPC/CAN

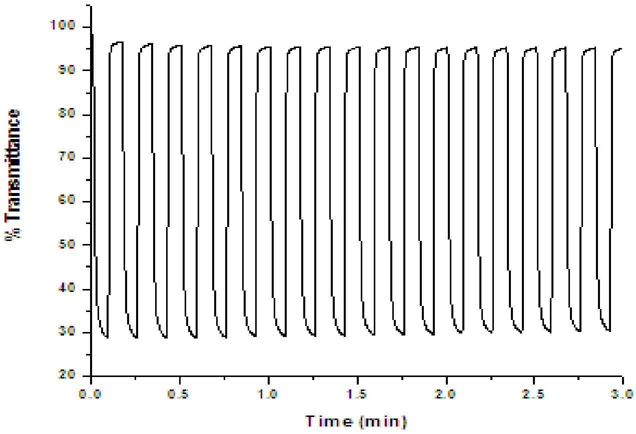


Figure 3. 17 Electrochromic switching, percent transmittance change monitored at 1300 nm for SEBTSE in 0.1 M TBAPC/CAN

PSEBTSE	**580 nm**	**1300 nm**
Optical contrast	**24 %**	**71 %**
Switching time	**1.1 sec**	**0.9 sec**

Table 3. 2 Optical contrasts and related switching times of PSEBTSE

CHAPTER 4

CONCLUSION

The D-A-D type monomers; SEBTSE and PYBTPY were synthesized via bromination, stannylation and the Stille coupling. Characterizations of the materials were performed by NMR analysis. The polymers of the both monomers were synthesized by electrochemical methods. Cyclic voltammetry experiments, spectroelectrochemistry, kinetic studies and long-term switching experiments for the polymers were performed in order to investigate the electrochemical and electrochromic properties of the polymers.

Use of pyrrole and selenophene as the electron-rich units and benzothiodiazole as the electron deficient unit results in reducing the electronic band gap of the polymer significantly. The great donation ability of pyrrole makes the lowering much better than selenophene and thiophene units do.

Since electrochromic materials are used in wide applications, synthesis of their different derivatives is still important. As well as RGB, CMYK and some other special colors are vital for practical uses. To have a great knowledge about a monomer, detailed information about its structure is needed. Therefore this study was performed to compare donor groups of a D-A-D monomer.

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